U.S. DEPARTMENT OF COMMERCE
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PB-273 349

Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters

Illinois Univ at Urbana-Champaign

Prepared for

Environmental Protection Agency, Washington, D C

stances

Jul 77

EPA-
560/6-77-015

PB 273 349

MONITORING TO DETECT PREVIOUSLY UNRECOGNIZED POLLUTANTS IN SURFACE WATER

July 1977

Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

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TECHNICAL REPORT DATA
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EPA-560/6-77-015	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters		5. REPORT DATE July 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) B. B. Ewing, E. S. K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, and F. G. Perkins		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Institute for Environmental Studies 408 S. Goodwin Avenue University of Illinois at Urbana-Champaign Urbana, Illinois 61801		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. EPA 68-01-3234
12. SPONSORING AGENCY NAME AND ADDRESS United States Environmental Protection Agency Office of Toxic Substances Washington, D. C. 20460		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE 560/06

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Samples of surface waters were collected from 204 sites near heavily industrialized areas across the United States. The samples were analyzed for all contaminants present at concentrations greater than one part per billion. Each water sample was preconcentrated for analysis of organics in three fractions: volatile organics by nitrogen-gas stripping and the less-volatile organics by extraction with chloroform under both basic and acidic conditions. Organic constituents were identified by gas chromatography/mass spectrometry and quantified by gas-chromatographic techniques. Inorganic constituents were determined by spark-source mass spectrometry, energy-dispersive x-ray fluorescence analysis, and instrumental neutron activation analysis. For comparison with previous data from the same sites, the samples were also analyzed for total chemical oxygen demand, turbidity, conductivity, pH, color, oxidation-reduction potential, suspended solids, and volatile suspended solids. Results of the inorganic analyses were presented in previous quarterly progress reports. Final results of the organic analyses are presented in the appendix to this report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Water quality Water pollution Water analysis Water chemistry Surface waters	Trace contaminants Organic compounds Volatile organic compounds Industrial pollution Nationwide survey	8h 7b, 7c, 7e

18. DISTRIBUTION STATEMENT Unrestricted Available from National Technical Information Service, Springfield, VA 22151	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 89 22. PRICE PCA05-A01

EPA Form 2220-1 (9-73)

EPA-560/6-77-015

MONITORING TO DETECT PREVIOUSLY UNRECOGNIZED POLLUTANTS IN SURFACE WATERS

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Final Report
Contract No. 68-01-3234

July 1977

Project Officer--Vincent J. DeCarlo

Prepared for

Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C. 20460

Document is available to the public through the National Technical Information Service, Springfield, Virginia 22151

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ACKNOWLEDGMENTS

The Institute for Environmental Studies and the project team members express their appreciation to Dr. Larry Keith, formerly of the USEPA laboratory in Athens, Georgia, to Dr. John McGuire of the Athens laboratory, and to Dr. Billy Fairless of the USEPA Region V office for valuable advice on the refinement of sample preparation and analysis techniques. Gratitude is also expressed to the many local, state, and federal officials whose cooperation greatly facilitated the process of locating sampling sites and collecting samples.

1. INTRODUCTION

This report summarizes the activities and accomplishments of a research project conducted to detect previously unrecognized pollutants in surface waters. The work was supported by the U. S. Environmental Protection Agency under Contract No. 68-01-3234.

BACKGROUND AND OBJECTIVES

The heavy concentration of industry in certain areas of the United States has caused increasing concern about the introduction of contaminants into our surface waters, especially since some constituents of industrial waste discharges have proven to be carcinogenic or toxic at trace levels. With the proliferation of new chemical substances it is likely that some potentially harmful pollutants in our surface waters have gone undetected. At the same time as waste discharges to our waterways have increased, we have come to rely more heavily on those water resources not only for industrial but also for municipal water supplies. It was therefore deemed vital to detect contaminants wherever they may be present.

The purpose of the present study was to undertake a sampling and analytical survey to determine, insofar as possible, the identities and semiquantitative concentrations of organic compounds and inorganic elements present in the waterways around industrial centers in the United States.

A total of 204 water samples were collected from fourteen heavily industrialized river basins. These areas and the number of samples taken from each are indicated in Figure 1. Each sample was analyzed using state-of-the-art techniques for detecting trace contaminants.

ORGANIZATION

This interdisciplinary project, conducted at the University of Illinois at Urbana-Champaign, was administered by the Institute for Environmental Studies.

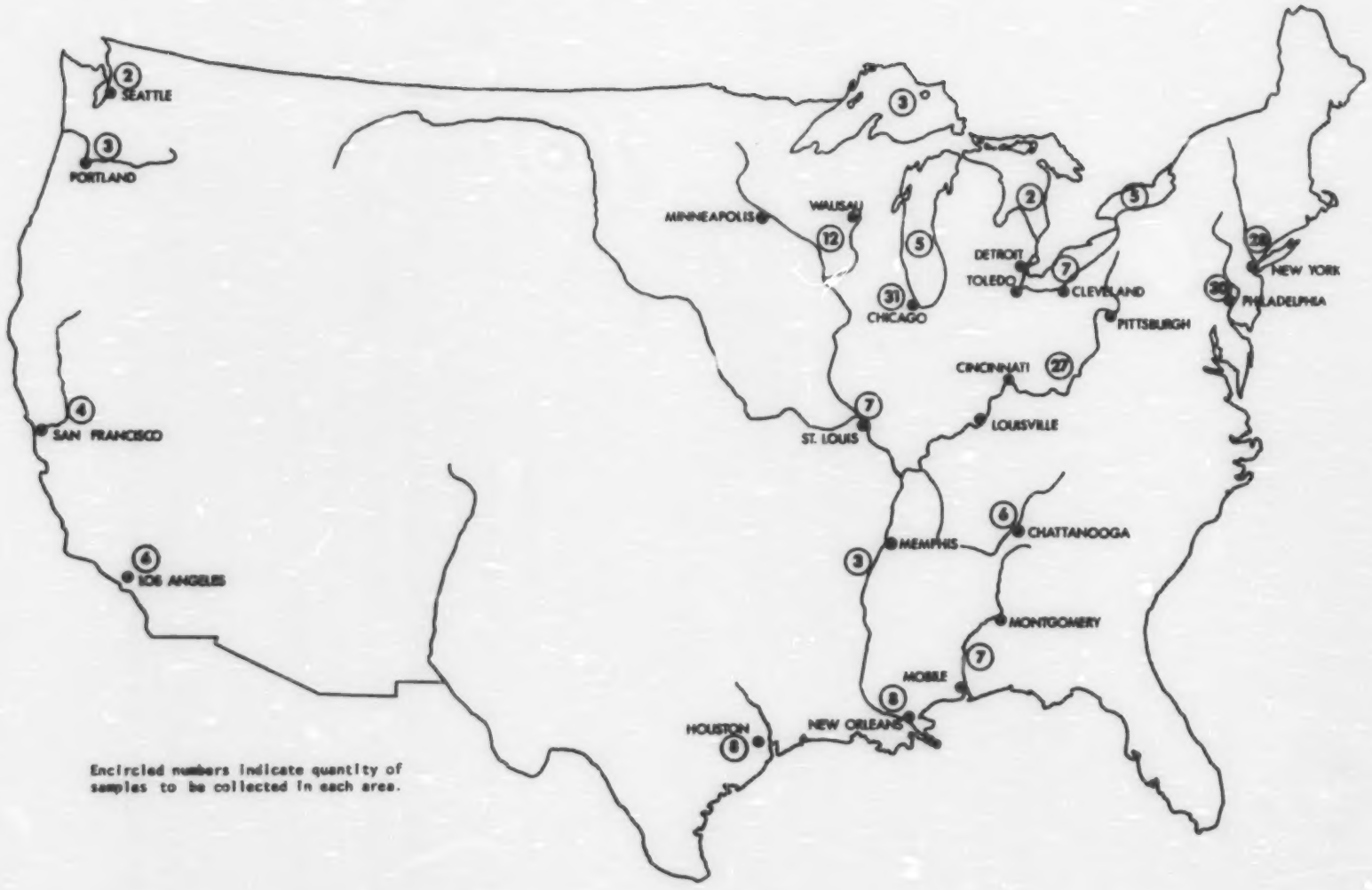

Figure 1. Industrialized areas sampled.

It involved the personnel and facilities of five university units. The project was directed by the co-principal investigators, Professor E. S. K. Chian, Department of Civil Engineering, and Professor B. B. Ewing, Director of the Institute. The participating units and principal research personnel were:

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SAMPLE COLLECTION AND ANALYSIS SCHEDULE

The research contract was executed for initiation on July 1, 1975, for an 18-month period to terminate December 31, 1976. The first six samples were collected in the Chicago area in August 1975. The initial six months of the project were devoted to staffing, development of methods, and the analysis of these six samples. The sampling rate was then increased so that all sampling would be completed by September 1976 and was adjusted as necessary to keep sample collections only moderately in advance of the analysis process. The sampling schedule for the entire project is shown in Figure 2. All samples were numbered in the chronological sequence of collection.

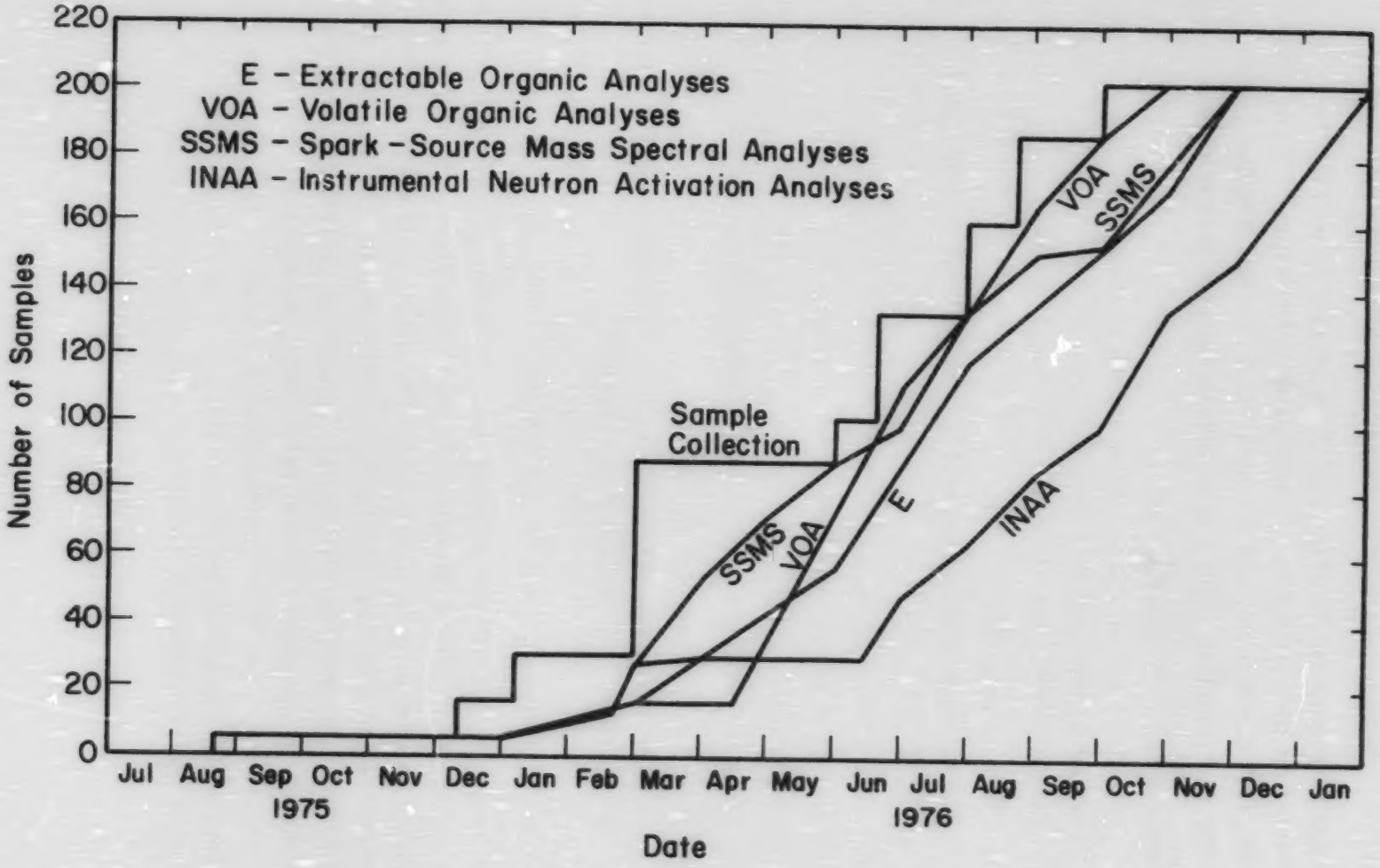

Figure 2. Sample collection and analysis schedule.

Inorganic analyses by x-ray fluorescence and spark-source mass spectrometry were completed at a rate of approximately 20 samples per month, closely following the delivery of the samples to the University of Illinois campus. It was intended that instrumental neutron activation analysis be performed at the same rate, but after processing 28 samples the schedule was delayed for about three months because of an equipment failure.

Analysis for volatile organics was delayed a few months after processing the initial six samples so that the methodology could be revised to improve detection limits. Thereafter, the rate of analysis was increased to about 30 samples per month until the backlog was reduced, after which it followed the sampling schedule closely. The preparation and analysis of extractable organics generally followed the collection schedule throughout the last 12 months of the project. The organic and inorganic analysis schedules are also shown in Figure 2.

2. SITE SELECTION, SAMPLE COLLECTION, AND GROSS ANALYSIS

SITE SELECTION

E. S. K. Chian
F. B. DeWalle

During the study, water samples were collected from 204 sites across the continental United States. The areas sampled and the number of samples collected in each are indicated in Figure 1. The sites were chosen in such a way that the concentration of organic and inorganic contaminants in the collected water samples would be affected by industrial pollutants and so that all principal types of industry would be represented. So that the impact of industrial discharges on water quality could be assessed, a limited number of samples were generally taken upstream from industrial sources in the less polluted reaches of rivers while the majority of the samples were collected from the waterways near major industrial areas. Several downstream sites were also sampled to indicate the extent to which contaminant concentrations were attenuated.

The samples were generally taken at sampling locations established by state or federal water pollution regulatory agencies. The sites are listed in Tables 1 through 7 along with the coordinates and description of their locations. The maps presented in Figures 3 through 17 show the general position of each site along the waterways sampled.

Ninety-one of the sites were located along major rivers such as the Hudson, the Delaware, the Mississippi, the Ohio, and the Tennessee. Fifty-seven samples were collected in tidal areas and estuaries, such as the Hudson River estuary, the Delaware River estuary, Mobile Bay, Galveston Bay, Los Angeles Harbor, San Francisco Bay, and Puget Sound. Twelve sites were located in manmade canals and three in major lakes. Since industrial wastewater is often treated at municipal sewage treatment plants, four samples were taken from effluent discharge structures.

Table 1

Sampling Sites in the Chicago Area and the Illinois River Basin

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
1	---	WSW Sewage Treatment Plant	41.48.51	87.46.11	Pershing & Austin Roads	Stickney, IL	Final effluent after sec. sedimentation & chlorination
2	---	Chicago Central Water Wks	41.53.45	87.36.20	Lake Shore Drive & Ohio St.	Chicago, IL	Final tap water
3	Calumet-Sag Channel	Highway 83 Bridge	41.41.53	87.56.12	U.S. Highway 83	Lemont, IL	Midstream
4	Calumet-Sag Channel	Ashland Avenue Bridge	41.39.22	87.39.39	Ashland Avenue	Blue Island, IL	Midstream
5	Chicago Sanitary & Ship Canal	Lockport Powerhouse	41.34.08	88.04.41	---	Lockport, IL	From sideline of large water tunnel.
6	Chicago Sanitary & Ship Canal	Highway 83 Bridge	41.42.02	87.56.22	U.S. Highway 83	Lemont, IL	Midstream
7	---	Chicago Central Water Wks	41.53.45	87.36.20	Lake Shore Drive & Ohio St.	Chicago, IL	Untreated L. Michigan Wtr.
8	---	Chicago Central Water Wks	41.53.45	87.36.20	Lake Shore Drive & Ohio St.	Chicago, IL	Final tap water after chlorination
9	Chicago Sanitary & Ship Canal	Lockport Powerhouse	41.34.08	88.04.41	---	Lockport, IL	Tunnel water (field extracted & stripped)
10	---	North Side Sewage Treatment Plant	42.01.11	87.42.42	Howard and McCormick Blvd.	Lincolnwood, IL	Final effluent after chlorination
11	---	West Side Sewage Treatment Plant	41.48.51	87.46.11	Pershing and Austin Roads	Stickney, IL	Final effluent after chlorination
12	---	Calumet Sewage Treatment Plant	41.39.36	87.44.23	130th St. & Lawrence Ave.	Chicago, IL	Final effluent after chlorination
13	---	South West Filtration Plant	41.47.10	87.32.00	South Shore Dr. & Chattenham	Chicago, IL	Final tap water after chlorination
14	Indiana Harbor Cnl.	Indiana Harbor	41.39.19	87.27.34	Dickey Road	E. Chicago, IN	Midstream
15	Calumet River	Calumet River	41.39.36	87.44.23	130th Street Bridge	Chicago, IL	Midstream
16	Calumet-Sag Channel	Ashland Avenue Bridge	41.39.22	87.39.39	Ashland Avenue	Blue Island, IL	Midstream
17	Calumet-Sag Channel	Highway 83 Bridge	41.41.53	87.56.12	U.S. Highway 83	Lemont, IL	Midstream
18	---	Chicago Central Water Wks	41.53.45	87.36.20	Lake Shore Drive & Ohio St.	Chicago, IL	Final tap water (XAD, carbon extractions)
19	Chicago Sanitary & Ship Canal	Lockport Powerhouse	41.34.08	88.04.41	---	Lockport, IL	Tunnel water (XAS, carbon extractions)
20	Calumet River	Highway 41 Bridge	41.43.37	87.42.30	U.S. Highway 83	Chicago, IL	Near mouth, midstream
21	Calumet-Sag Channel	Ashland Avenue Bridge	41.39.22	87.39.39	Ashland Avenue	Blue Island, IL	Midstream
22	Des Plaines River	Des Plaines River	41.25.25	88.11.35	U.S. Highway 55	Elwood, IL	Midstream
23	Illinois River	Dresden Island Lock & Dam	41.23.53	88.16.45	---	Dresden, IL	Midstream
24	Illinois River	Utica, Illinois	41.19.29	89.02.00	U. S. Highway 178	Utica, IL	Midstream
25	Illinois River	Hennepin, Illinois	41.15.00	89.23.00	U. S. Highway 26	Hennepin, IL	Midstream
26	Illinois River	Peoria Water Works	40.43.30	89.33.10	---	Peoria, IL	Untreated river water
27	---	Peoria Water Works	40.43.30	89.33.10	---	Peoria, IL	Finished water
28	Illinois River	Pekin, Illinois	40.34.25	89.39.15	U. S. Highway 9	Pekin, IL	Midstream
29	Illinois River	Havana, Illinois	40.18.00	90.04.00	U. S. Highway 97	Havana, IL	Midstream
30	Illinois River	Meredosia, Illinois	39.50.00	90.34.00	U. S. Highway 104	Meredosia, IL	Midstream
31	Illinois River	Hardin, Illinois	39.10.00	90.37.00	U. S. Highway 100	Hardin, IL	Midstream

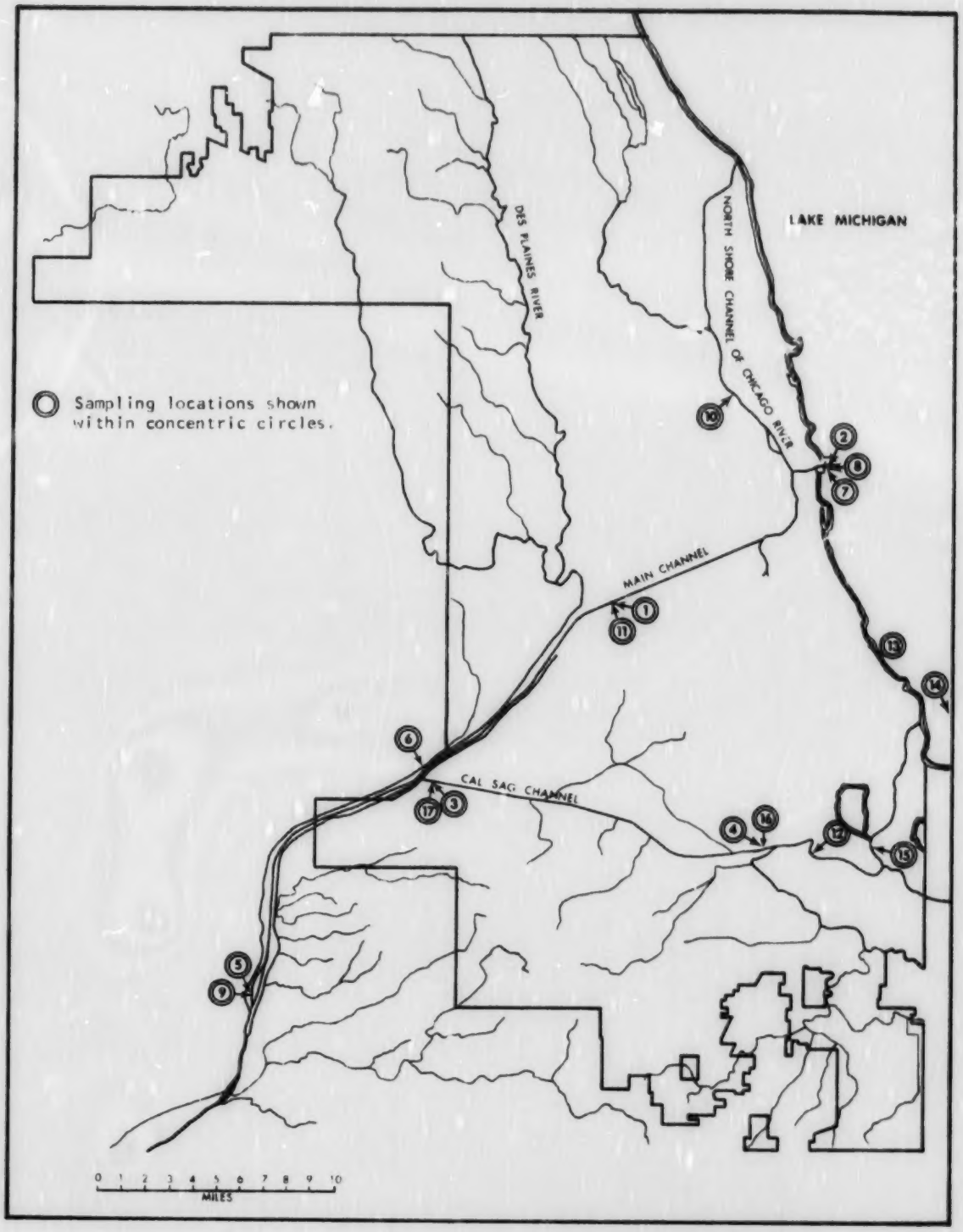
LAKE MICHIGAN
DES PLAINES RIVER
NORTH SHORE CHANNEL OF CHICAGO RIVER
MAIN CHANNEL
CAL SAG CHANNEL
Sampling locations shown within concentric circles.
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Figure 3. Sites sampled in the Chicago metropolitan area.

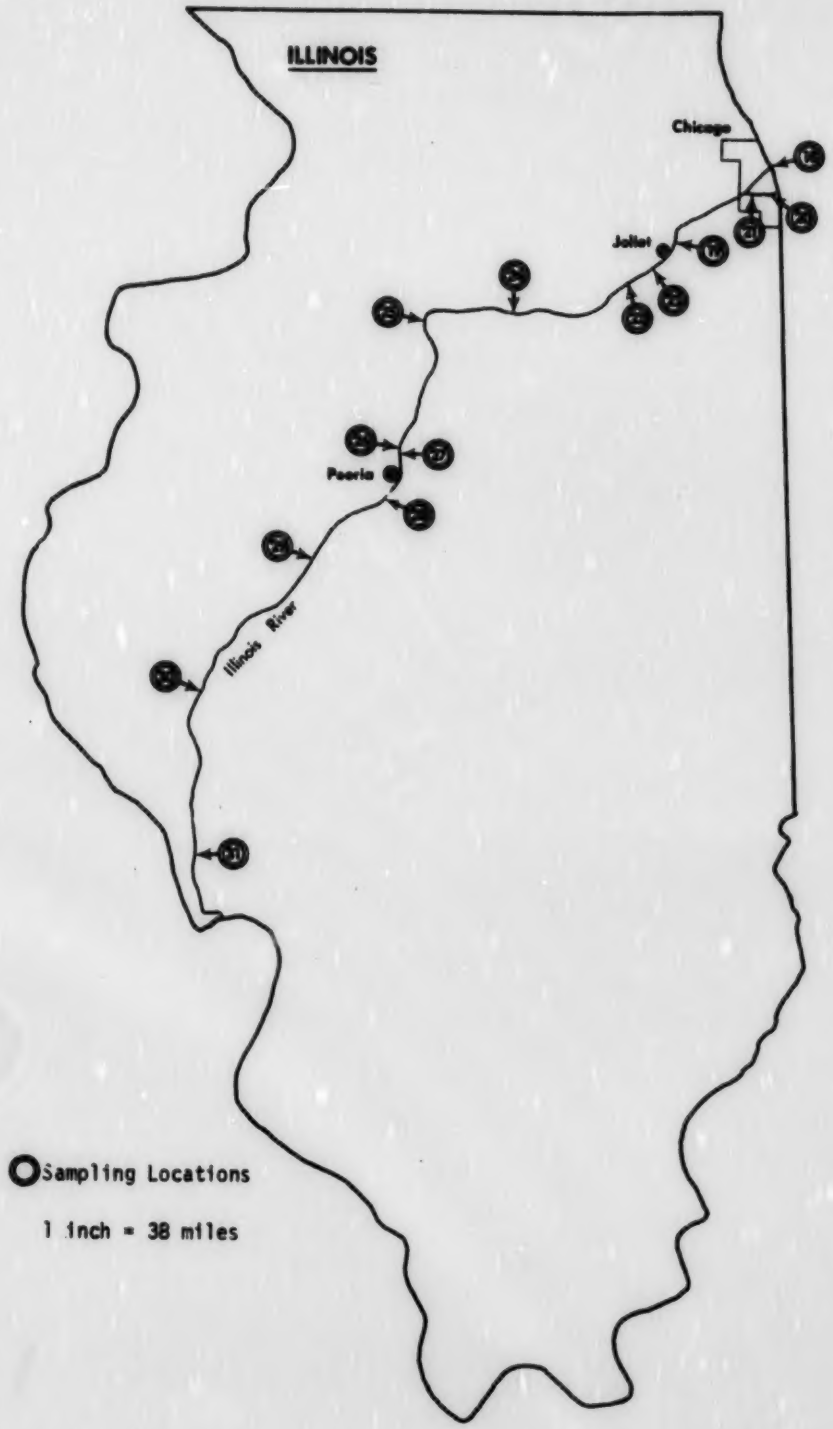

Figure 4. Sites sampled in the Illinois River basin.

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Table 2

Sampling Sites in the Delaware River Basin

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
32	Delaware River	St. John	39.18.14	75.22.57	Bombay Hook Pt.	Woodland Beach,DE	mid channel; low slack tide
33	Delaware River	Reedy Island	39.30.46	75.33.12	---	Port Penn, DE	mid channel; low slack tide
34	Delaware River	D. Memorial Bridge	39.42.35	75.32.13	U.S. Highway 295	Pigeon Point, DE	mid channel; low slack tide
35	Delaware River	Marcus Hook	39.47.55	75.25.48	Blue Ball Avenue	Marcus Hook, PA	mid channel; low slack tide
36	Delaware River	Paulsboro	39.50.54	75.15.53	Little Tinicum Island	Paulsboro, NJ	mid channel; low slack tide
37	Delaware River	Navy Yard	39.52.39	75.11.45	West Horseshoe Range	Philadelphia, PA	mid channel; low slack tide
38	Delaware River	B. Franklin Bridge	39.57.10	75.08.10	U.S. Highway 676	Philadelphia, PA	mid channel; low slack tide
39	Delaware River	Five Mile Point	39.58.40	75.04.35	Frankford Creek	Bridesburg, PA	mid channel; low slack tide
40	Delaware River	Torresdale Range	40.02.00	74.59.20	Pennypack Creek	Torresdale, PA	mid channel; low slack tide
41	Delaware River	Bristol	40.05.13	74.51.12	Otter Creek	Bristol, PA	mid channel; low slack tide
42	Delaware River	D. Memorial Bridge	39.42.35	75.32.13	U.S. Highway 295	Pigeon Point, DE	mid channel; high slack tide
43	Delaware River	Mouth	38.49.60	75.01.40	Cape Henlopen	Lewes, DE	mid channel; high slack tide
44	Delaware River	Mouth	38.58.53	75.07.42	Brandywine Shoal	Fowlers Beach, DE	mid channel; high slack tide
45	Delaware River	Mouth	39.03.03	75.10.00	Fourteen Foot Bank	Big Stone Beach, DE	mid channel; high slack tide
46	Delaware River	Mouth	39.10.50	75.16.24	Elbow of Cross Ledge	Pickering Beach, DE	mid channel; high slack tide
47	Delaware River	Margaretville	42.22.42	74.32.18	McGregor Mnt. on U.S. Hwy 30	Margaretville, DE	mid channel; high slack tide
48	Delaware River	St. John	39.18.14	75.22.57	Bombay Hook Point	Woodland Beach, DE	mid channel; high slack tide
49	Schuylkill River	Mouth	39.53.24	75.11.45	Reserve Basin	Philadelphia, PA	mid channel; low slack tide
50	Schuylkill River	Queens Lane	39.58.00	75.11.05	U.S. Hwy 1 to U.S. Hwy 76	Philadelphia, PA	mid channel; non tidal
51	Schuylkill River	Queens Lane	39.58.00	75.11.05	U.S. Hwy 1 to U.S. Hwy 76	Philadelphia, PA	mid channel; finished water
52	Delaware River	Torresdale	40.02.24	74.59.40	City Water Treatment Plant	Torresdale, PA	mid channel; high slack tide
53	Delaware River	Torresdale	40.02.24	74.59.40	City Water Treatment Plant	Torresdale, PA	mid channel; finished water
54	Lehigh River	Allentown	40.37.22	75.28.57	Tilghman Street	Allentown, PA	mid channel; non tidal
55	Lehigh River	Hill to Hill	40.36.58	75.22.40	Wyandelle Ave., P.S. Hwy 378	Bethlehem, PA	mid channel; non tidal
56	Lehigh River	Bethlehem	40.37.11	75.20.11	Freemonsburg Bridge	Bethlehem, PA	mid channel; non tidal
57	Lehigh River	Easton	40.41.13	75.12.32	S. Delaware St., P.S. Hwy 611	Easton, PA	mid channel; non tidal
58	Delaware River	Easton	40.42.43	75.11.48	N. Delaware Drive, City WTP	Easton, PA	mid channel; non tidal
59	Delaware River	Trenton	40.13.17	74.46.44	City WTP, P.S. Hwy 29	Trenton, NJ	mid channel; non tidal
60	Delaware River	Trenton	40.13.17	74.46.44	City WTP, P.S. Hwy 29	Trenton, NJ	mid channel; finished water
61	Delaware River	Frenchtown	40.31.40	75.04.00	N.J.S. Hwy 12	Frenchtown, NJ	mid channel; non tidal

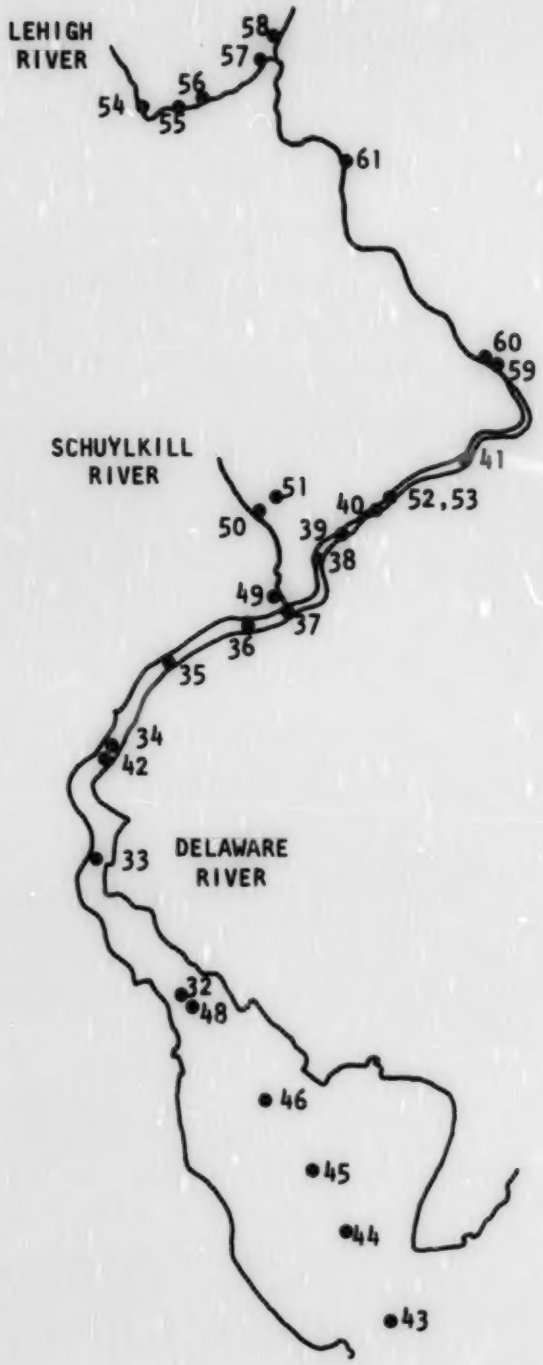

Figure 5. Sites sampled in the Delaware River basin.

Table 3

Sampling Sites in the Hudson River Basin

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
62	Raritan Bay	Perth Amboy	40.29.12	74.14.21	Ward Point Bent	Tottenville, NY	mid channel; low slack tide
63	Raritan Bay	Perth Amboy	40.29.40	74.16.52	CRR of N.J. RRB at Sandy Pt.	Perth Amboy, NJ	mid channel; low slack tide
64	Arthur Kill	Perth Amboy	40.30.44	74.15.34	Ferry Dock	Perth Amboy, NJ	mid channel; low slack tide
65	Arthur Kill	Sewaren	40.33.05	74.15.00	Smith Creek	Sewaren, NJ	mid channel; low slack tide
66	Arthur Kill	Tufts Point	40.34.42	74.13.00	Fresh Kills	Chrome, NJ	mid channel; low slack tide
67	Arthur Kill	Tremley Point	40.36.17	74.12.08	Pralls Island	Graselli, NJ	mid channel; low slack tide
68	Arthur Kill	Port Elizabeth	40.38.47	74.10.42	North of Shooter's Range	Port Elizabeth, NJ	mid channel; low slack tide
69	Newark Bay	Newark	40.39.17	74.08.47	CRR of N.J. RRB, Bergen Pt.	Newark, NJ	mid channel; low slack tide
70	Hudson River	Bayonne	40.39.11	74.03.43	Robbins Reef	Bayonne, NJ	mid channel; low slack tide
71	Hudson River	Narrows	40.36.20	74.02.45	Verrazano Bridge, U.S. 278	Rosebank, NY	mid channel; low slack tide
72	Hudson River	Lower Bay	40.32.10	74.01.35	Romer Shoal	Sandy Hook, NJ	mid channel; low slack tide
73	Hudson River	Beacon	41.30.18	74.59.21	Main Street	Beacon, NY	shore sample; low slack tide
74	Hudson River	Poughkeepsie	41.44.05	73.56.15	City Water Treatment Plant	Poughkeepsie, NY	shore sample; low slack tide
75	Hudson River	Poughkeepsie	41.44.05	73.56.15	City Water Treatment Plant	Poughkeepsie, NY	finished water
76	Hudson River	Kingston	41.55.40	73.57.44	N.Y.S. Hwy 30	Kingston, NY	shore sample; low slack tide
77	Hudson River	Catskill	42.12.36	73.51.12	N.Y.S. Hwy 385	Catskill, NY	shore sample; low slack tide
78	Hudson River	Glenmont	42.35.43	73.45.43	Elect. Power & Light Co.	Glenmont, NY	shore sample; low slack tide
79	Hudson River	Waterford	42.47.50	73.40.33	N.Y.S. Hwy 32	Waterford, NY	mid channel; non tidal
80	Hudson River	Thomson	43.07.36	73.35.16	U.S. Hwy 4	Thomson, NY	mid channel; non tidal
81	Hudson River	Glens Falls	43.18.20	73.36.58	N.Y.S. Hwy 32	Glens Falls, NY	mid channel; non tidal
82	Hudson River	Corinth	43.14.53	73.49.49	N.Y.S. Hwy 9N	Corinth, NY	mid channel; non tidal
83	Mohawk River	Schenectady	42.49.07	73.56.59	N.Y.S. Hwy 50	Schenectady, NY	shore sample; non tidal
84	Mohawk River	Waterford	42.49.07	73.56.59	N.Y.S. Hwy 32	Waterford, NY	mid channel; non tidal
85	Passaic River	Mouth	40.43.54	74.07.04	Lincoln Hwy, U.S. Hwy 1/9	Newark, NJ	mid channel; low slack tide
86	Hackensack River	Mouth	40.43.39	74.05.57	Lincoln Hwy, U.S. Hwy 1/9	Jersey City, NJ	mid channel; low slack tide
87	Hudson River	Fort Lee	40.50.37	73.58.03	N.Y.S. Hwy 505	Fort Lee, NJ	shore sample; low slack tide
88	Hudson River	Piermont	41.02.34	73.53.48	Continental Can Dock	Piermont, NY	shore sample; low slack tide
89	Hudson River	Iona	41.18.51	73.59.08	Bear Mountain Bridge	Ft. Montgomery, NY	shore sample; low slack tide

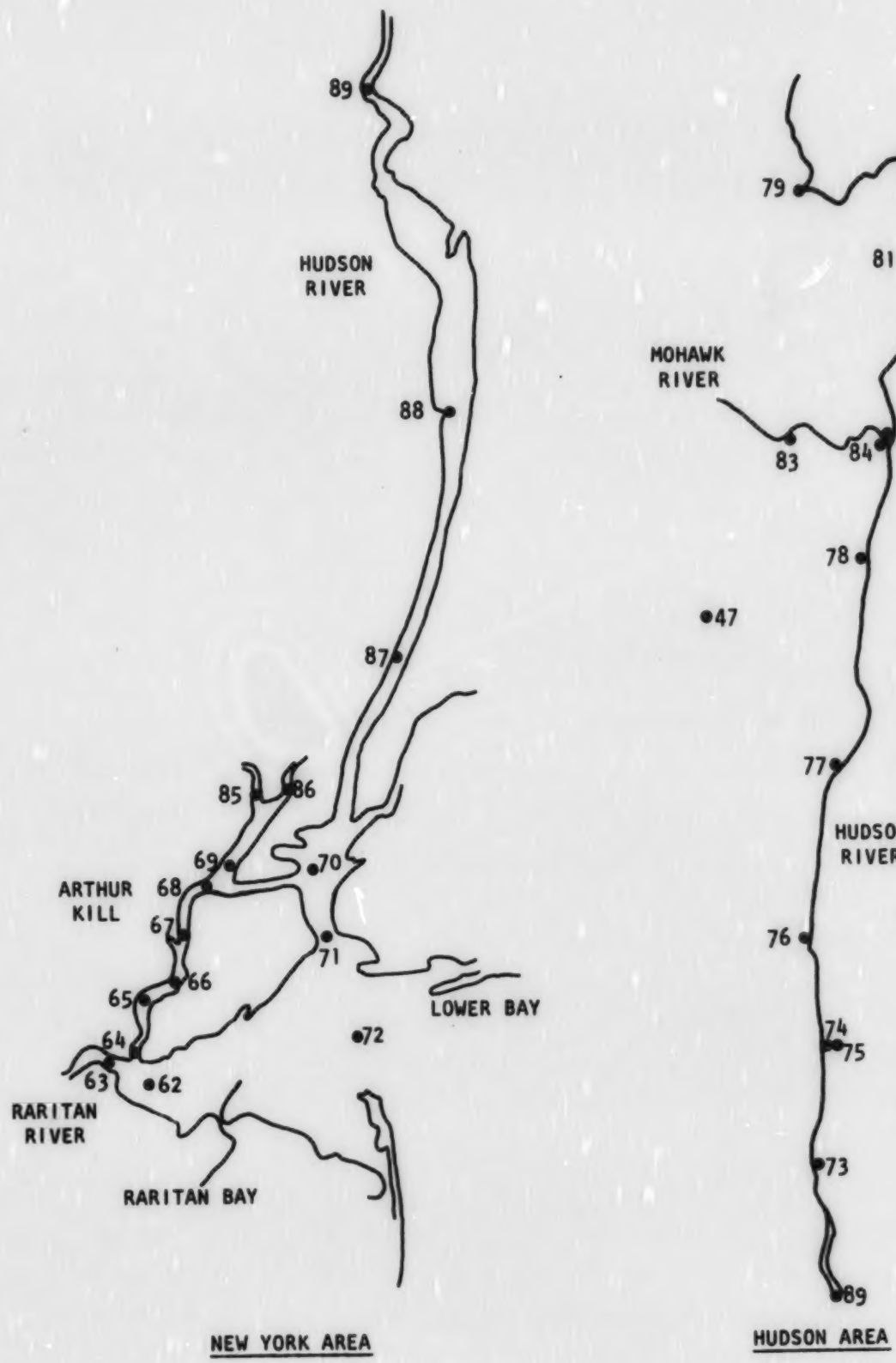

Figure 6. Sites sampled in the Hudson River basin.

Table 4

Sampling Sites in the Mississippi River Basin, in Alabama, and in Texas

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
90	Mississippi River	State Highway 6	46.32.40	93.57.09	M.S. Hwy 6	Crosby, MN	Midchannel
91	"	Fourth St., Minneapolis	44.51.12	93.00.35	4th Ave. and County Hwy 24	Inver Grove Heights,MN	Midchannel
92	"	Wabash St., Minneapolis	44.56.40	93.05.19	Wabash St.	St. Paul, MN	Midchannel
93	"	St. Paul Intake	45.07.33	93.16.36	Talmadge Lane	Fridley, MN	Shore
94	"	St. Paul Finished Water	45.00.10	93.10.50	Roselawn	Maplewood, MN	Roseville
95	"	Lock and Dam 3	44.36.40	92.36.42	U.S. Hwy 63	Red Wing, MN	Midchannel
96	"	Reads Landing	44.24.45	92.06.47	U.S. Hwy 61	Reeds Landing, MN	Midchannel
97	"	Weaver Bottom	44.12.29	91.47.45	U.S. Hwy 61	Weaver, MN	Midchannel
98	"	Lower Weaver Bottom	44.12.26	91.47.43	U.S. Hwy 61	Weaver, MN	Near shore
99	Wisconsin River	Wausau	44.56.55	89.37.34	W.S. Hwy 52	Wausau, WI	Midchannel
100	"	Nekoosa	44.17.46	89.53.97	Above Munic. STP	Nekoosa, WI	Midchannel
101	"	Bridgeport	43.00.00	91.03.00	U.S. Hwy 18	Bridgeport, WI	Midchannel
102	Buffalo Bayou	Shepard Dr.	29.45.30	95.22.36	---	Houston, TX	Midchannel
103	Houston Ship Channel	Morgan Point	29.40.24	94.58.42	Main Street	Morgan Point, TX	Midchannel
104	"	Lynchburg Ferry	29.45.39	95.04.25	T.S. Hwy 134	Lynchburg, TX	Midchannel
105	"	Tuckers Bayou	29.44.30	95.11.18	Tidal Road	Deer Park, TX	Midchannel
106	"	North Shaver Road	29.43.24	95.13.12	N. Shaver Rd., County 526	Pasadena Gardens, TX	Midchannel
107	"	Turning Basin	29.44.54	95.17.12	75th Street	Magnolia Park, TX	Midchannel
108	Galveston Bay	Pelican Island	29.21.54	94.47.46	T.S. Hwy 87	Galveston, TX	Midchannel
109	"	Red Fish Bay	29.29.37	94.51.52	Eagle Point	San Leon, TX	Midchannel
110	Mississippi River	Head of Passes	29.09.08	89.15.06	---	Venice, LA	Midchannel
111	"	Port Sulphur	29.28.39	89.41.21	M.S. Hwy 23	Port Sulphur, LA	Midchannel
112	"	Luling	29.56.19	90.21.40	Ferry Crossing M.S.Hwy 18 & 44	Luling, LA	Midchannel
113	"	Lutcher	30.01.55	90.41.45	Ferry Crossing M.S.Hwy 18 & 44	Lutcher, LA	Midchannel
114	"	New Orleans	29.57.03	90.08.17	Eagle/Spruce	New Orleans, LA	Shore
115	"	Finished Water	29.57.55	90.07.40	Eagle/Spruce	New Orleans, LA	Shore
116	"	Plaquemine	30.17.38	91.13.59	Ferry Crossing, M.S.Hwy 1 & 75	Plaquemine, LA	Midchannel
117	"	St. Francisville	30.45.30	91.23.45	Ferry Crossing, M.S. Hwy 10	St. Francisville, LA	Midchannel
118	Mobile Bay	Dauphin Island	30.06.35	88.02.11	Middle Ground	Dauphin Island, AL	Midchannel
119	"	Fowl River Pt.	30.29.30	88.01.06	Fowl River Point	Fowl River, AL	Midchannel
120	Mobile River	McDuffie Island	30.39.25	88.01.55	McDuffie Island	Mobile, AL	Midchannel
121	Black Warrior River	Demopolis	32.32.30	87.49.30	U.S. Hwy 43/SL,SF RRB	Demopolis, AL	Midchannel
122	"	Tuscaloosa	33.06.05	87.39.12	U.S. Hwy 11 and 43	Tuscaloosa, AL	Midchannel
123	"	Bankhead L.D.	33.27.36	87.21.12	Lock and Dam	Fosters, AL	Midchannel
124	"	Atwood Ferry	33.35.12	87.06.48	Atwood Ferry Bridge	Birmingham, AL	Midchannel
125	Mississippi River	Vicksburg	32.19.36	90.53.49	U.S. Hwy 80	Vicksburg, MS	Midchannel
126	"	Memphis	35.12.42	90.04.18	Loosahatchie River	Memphis, TN	Midchannel
127	"	Ensley Plantation	35.03.50	90.10.45	Arvid Power Line Crossing	Ensley Plantation, TN	Midchannel
128	"	St. Louis	38.42.06	90.15.00	Chain of Rocks Br.U.S. 270	St. Louis, MO	Shore
129	"	Finished Water	38.42.06	90.15.00	Chain of Rocks Br.U.S. 270	St. Louis, MO	Shore
130	"	Lock and Dam 26	38.53.48	90.14.36	U.S. Hwy 67	Alton, IL	Midchannel
131	Illinois River	Highway 100	39.09.24	90.41.36	I.S. Hwy 100	Hardin, IL	Midchannel
132	Mississippi River	Jefferson Barracks	38.29.10	90.16.28	U.S. Hwy 50	Mehlville, MO	Midchannel
133	"	Lock and Dam 14	41.32.36	90.24.30	I.S. Hwy 92	Muscatine, IA	Midchannel
134	"	Lock and Dam 16	41.27.24	91.00.00	U.S. Hwy 80	Davenport, IA	Midchannel

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Figure 7. Sites sampled on the upper and middle Mississippi River.

Figure 8. Sites sampled on the lower Mississippi River.

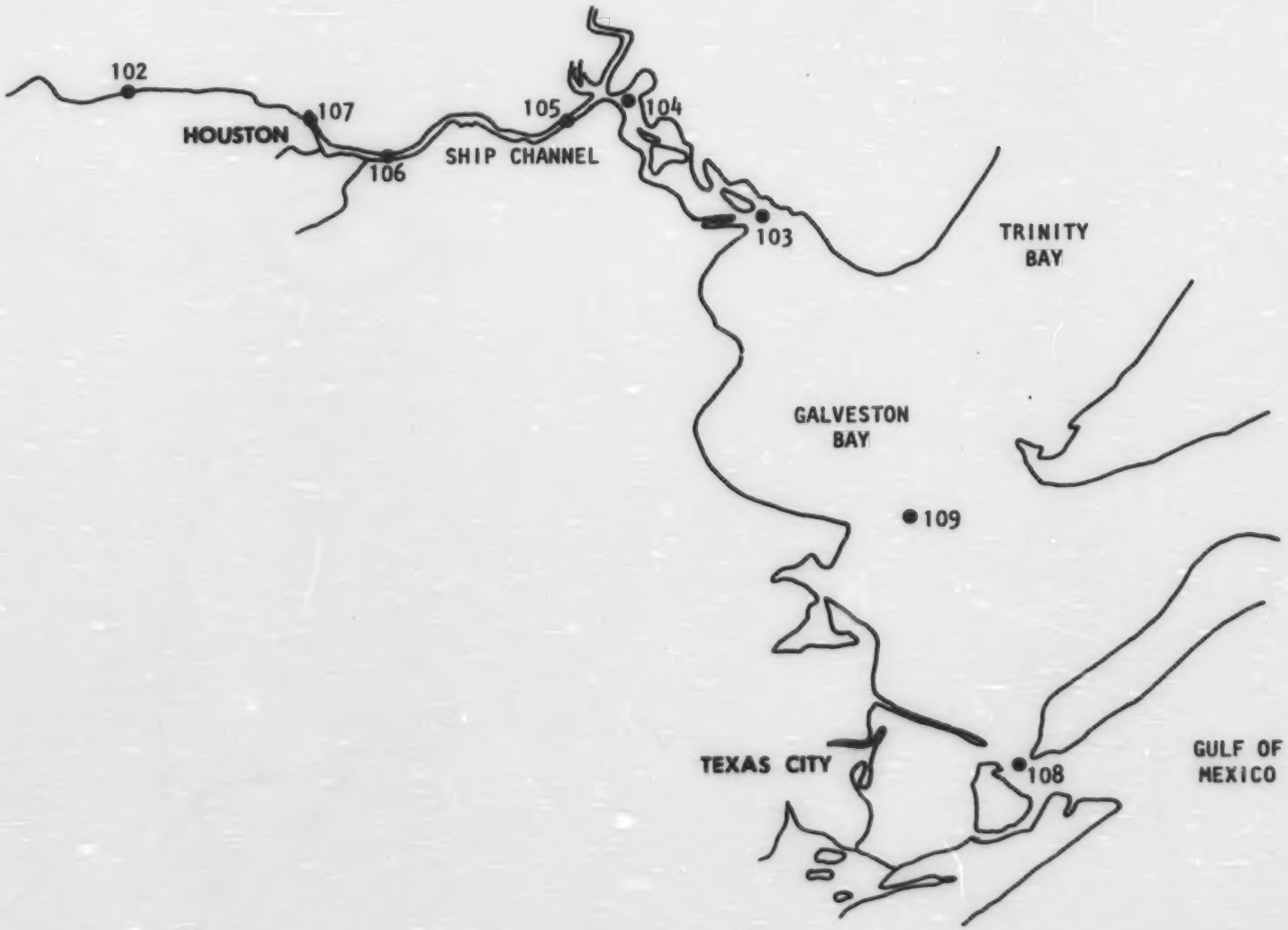


Figure 9. Sites sampled in the Houston area.

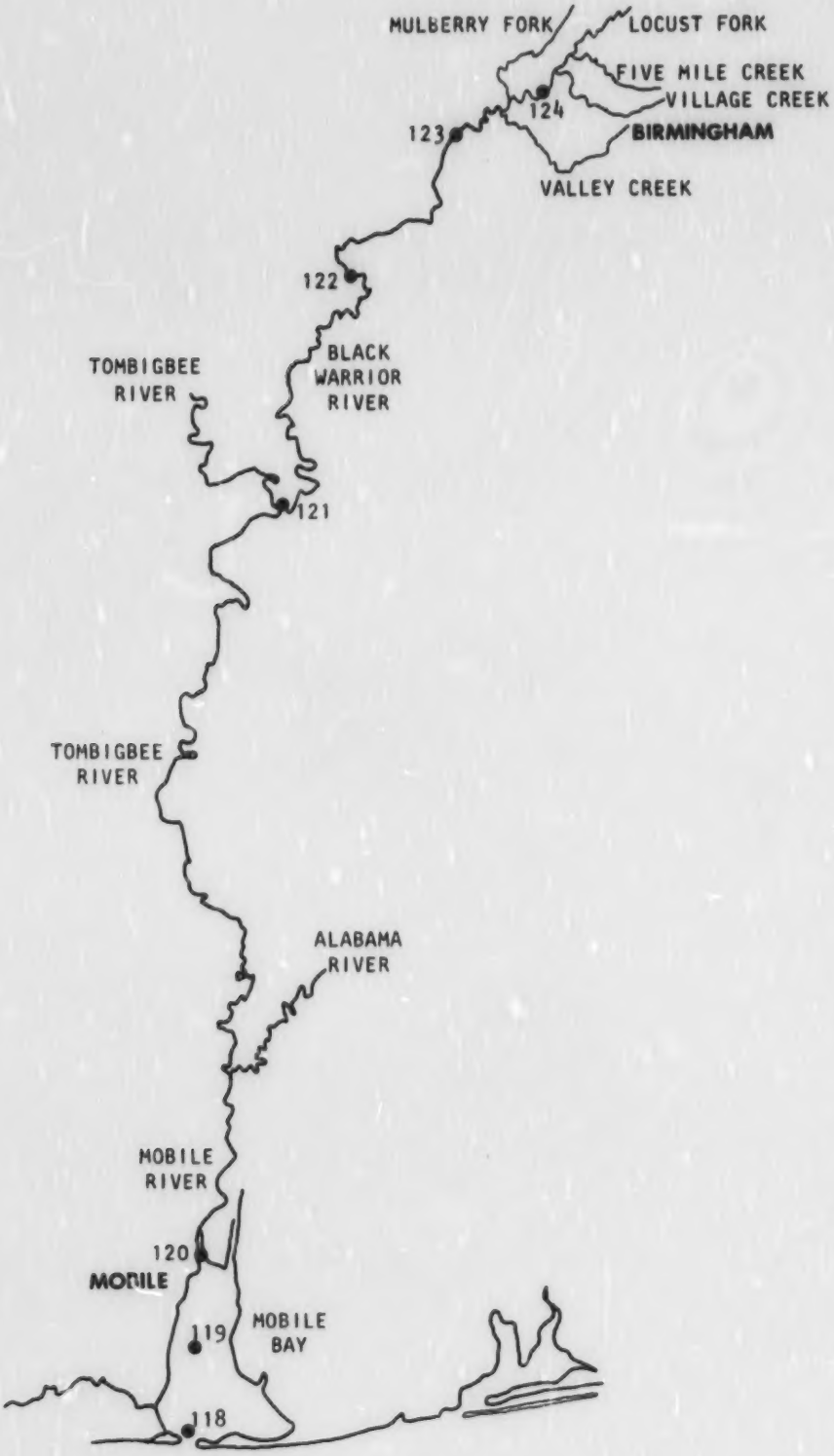


Figure 10. Sites sampled in Alabama.

Table 5

Sampling Sites in the Ohio River Basin

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
135	Ohio River	Joppa	37.12.00	88.51.00	Joppa Steam Plant	Joppa, IL	Midstream
136	Tennessee River	Calvert City	37.02.16	88.31.46	G.R. Clark Br., K.S. Hwy 60	Paducah, KY	Midstream
137	Wabash River	New Harmony	38.07.55	87.56.25	U.S. Hwy 460	New Harmony, IN	Midstream
138	Ohio River	Evansville WTP	37.58.20	87.34.35	Inland Marina Y.C.	Evansville, IN	Raw water
139	Ohio River	Evansville WTP	37.58.20	87.34.35	Inland Marina Y.C.	Evansville, IN	Finished water
140	Ohio River	Cannelton LD	37.53.53	86.42.20	Lock and Dam	Cannelton, IN	Midstream
141	Ohio River	Louisville WTP	38.16.52	85.42.08	Falls City Boat Company	Louisville, KY	Raw water
142	Kanawha River	Winfield	38.31.32	81.54.40	Lock and Dam	Winfield, WV	Midstream
143	Ohio River	Markland LD	38.46.29	84.57.52	Lock and Dam	Markland	Midstream
144	Ohio River	Cincinnati WTP	39.04.11	84.25.57	South of U.S. Hwy 275	Cincinnati, OH	Raw water
145	Ohio River	Cincinnati WTP	39.04.11	84.25.57	South of U.S. Hwy 275	Cincinnati, OH	Finished water
146	Ohio River	Huntington WTP	38.25.57	82.25.57	Tristate Materials Corp.	Huntington, WV	Raw water
147	Ohio River	Huntington WTP	38.25.57	82.25.57	Tristate Materials Corp.	Huntington, WV	Finished water
148	Ohio River	Belleville LD	39.07.07	81.44.32	Lock and Dam	Belleville, IL	Midstream
149	Ohio River	Joppa	37.12.00	88.51.00	Joppa Steam Plant	Joppa, IL	Midstream
150	Monongahela River	Point Marion	39.43.57	79.54.42	Upstream from Lock & Dam 8	Point Marion, PA	Midstream
151	Monongahela River	Charleroi	40.08.30	79.53.35	Belle Vernon Hwy Bridge	Charleroi, PA	Midstream
152	Allegheny River	Freeport LD	40.42.41	79.34.59	Above Lock & Dam 5	Freeport, PA	Midstream
153	Monongahela River	S. Pittsburgh WTP	40.24.36	79.57.15	Bedes Run	Pittsburgh, PA	Finished water
154	Monongahela River	S. Pittsburgh WTP	40.24.36	79.57.15	Bedes Run	Pittsburgh, PA	Raw water
155	Allegheny River	Oakmont WTP	40.31.51	79.50.12	Twelve Mile Island	Oakmont, PA	Raw water
156	Beaver River	Beaver Falls WTP	40.45.48	80.18.55	U.S. Hwy 18	Beaver Falls, PA	Finished water
157	Beaver River	Beaver Falls WTP	40.45.48	80.18.55	U.S. Hwy 18	Beaver Falls, PA	Raw water
158	Ohio River	South Heights	40.34.12	80.13.47	Duquesne Light Co. Intake	South Heights, PA	Midstream
159	Ohio River	E. Liverpool WTP	40.38.20	80.31.15	Mill Creek	E. Liverpool, OH	Finished water
160	Ohio River	E. Liverpool WTP	40.38.20	80.31.15	Mill Creek	E. Liverpool, OH	Raw water
161	Ohio River	Wheeling WTP	40.06.54	80.42.21	U.S. Army Base	Wheeling, WV	Raw water

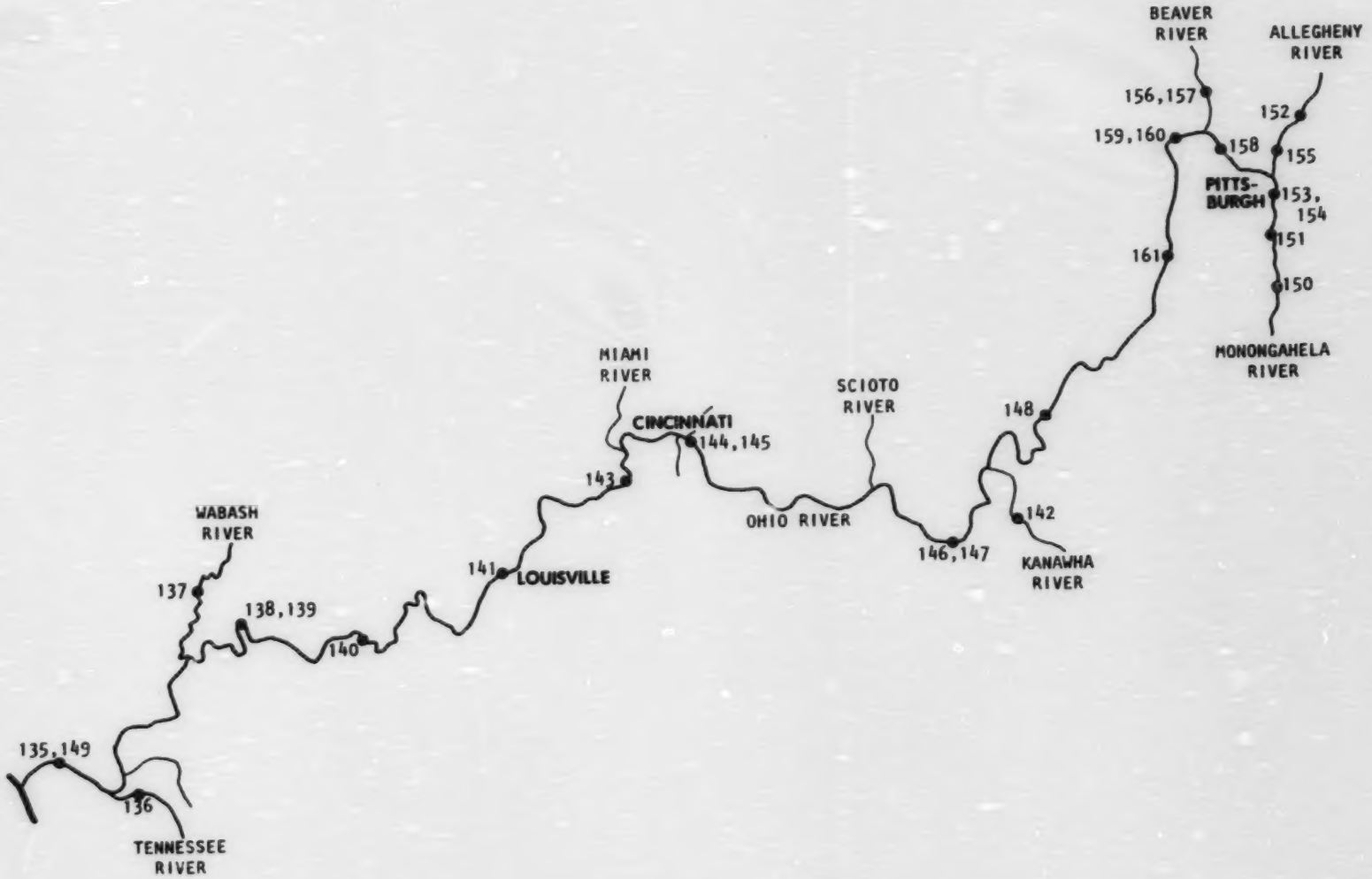


Figure 11. Sites sampled in the Ohio River basin.

Table 6

Sampling Sites in the Great Lakes and the Tennessee River Basin

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
162	St. Lawrence Seaway	Cape Vincent	44.07.58	76.20.40	Ferry to Alexandria	Cape Vincent, NY	Midstream
163	Black River	Dexter	44.00.15	76.02.39	N.Y. S. Hwy 180	Dexter, NY	Midstream
164	Oswego River	Oswego	43.27.23	76.30.35	U.S. Hwy 104	Oswego, NY	Midstream
165	Genessee River	Rochester	43.13.59	77.37.06	Turning Basin, Rattlesnake Pt.	Rochester, NY	Midstream
166	Niagara River	Fort Niagara	43.14.14	79.03.20	St. Catheriens Boat Club	Youngstown, NY	Midstream
167	Lake Erie	Buffalo	42.52.47	78.54.45	Middle Reefs Crib Intake	Buffalo, NY	Raw water
168	Fields Brook	Ashtabula	41.53.28	80.47.52	Riverside Yacht Club	Ashtabula, OH	Midstream
169	Cuyahoga River	Cleveland	41.29.15	81.41.11	W. 3rd St. near U.S. 71 & 90	Cleveland, OH	Midstream
170	Maumee River	Toledo	41.41.35	83.28.09	U.S. Hwy 65 Gage	Toledo, OH	Midstream
171	Detroit River	Maple Beach	42.03.20	83.11.35	Lee Rd. & Rockwood Drive	Gibraltar, MI	1/6 from shore
172	Detroit River	Detroit	42.16.21	83.06.32		Detroit, MI	1/6 from shore
173	St. Clair River	Port Huron	43.00.11	82.25.06	Ft. Gratiot Light	Port Huron, MI	Midstream
174	St. Clair River	Algonac	42.37.15	82.31.00	Ferry to Walpole Isl.	Algonac, MI	Midstream
175	Grand River	Grand Haven	43.03.35	86.14.36	Corps of Engineers Boatyard	Grand Haven, MI	Midstream
176	Saginaw River	Bay City	43.38.10	83.50.42	Corps of Engrs. Field Office	Bay City, MI	Midstream
177	Lake Michigan	Cecil Bay	43.45.35	84.45.00	One mile north of shore	Mackinaw City, MI	Midstream
178	St. Mary's River	Brush Point	46.28.46	84.26.58	Point aux Pins	Sault Ste. Marie, MI	Midstream
179	St. Louis River	Duluth	46.44.58	92.06.02	West Gate Basin, U.S. 535	Duluth, MN	Midstream
180	Lake Superior	Beaver Bay	47.16.00	91.16.42	Near munic. ramp, Pellet Isl.	Beaver Bay, WI	Near shore
181	Fox River	Green Bay	44.32.12	88.00.21	Green Bay Yacht Club	Green Bay, WI	Midstream
182	Milwaukee River	Milwaukee	43.01.29	87.54.01	U.S. 794, Evinrude Exp. St.	Milwaukee, WI	Midstream
183	Indiana Harbor Canal	Chicago	41.39.19	87.27.34	Dickey Place, Cty Hwy 912	East Chicago, IN	Midstream
184	French Broad	Asheville, N.C.	35.36.32	82.34.43	USGS Gaging Station, Rm* 144	Asheville, NC	Midstream
185	Holston River	Church Hill, Tenn.	36.31.00	82.43.22	Patterson Mill Br., Rm 131.5	Church Hill, TN	Midstream
186	Hiwassee River	Brittsville, Tenn.	35.22.03	84.54.35	I.S. Hwy 58 at Chickamonga L.	Brittsville, TN	Midstream
187	Ocoee River	Ducktown, Tenn.	35.00.13	84.24.22	Rogers Bridge	Ducktown, TN	Midstream
188	Chattanooga Creek	Chattanooga, Tenn.	35.01.08	85.19.35	L & N RR Bridge	Chattanooga, TN	Midstream
189	Tennessee River	Paducah, Ky.	37.02.16	88.31.46	Ashland Oil Terminal	Paducah, KY	Midstream

*Rm = Rivermile

Figure 12. Sites sampled in the Great Lakes and their tributaries.

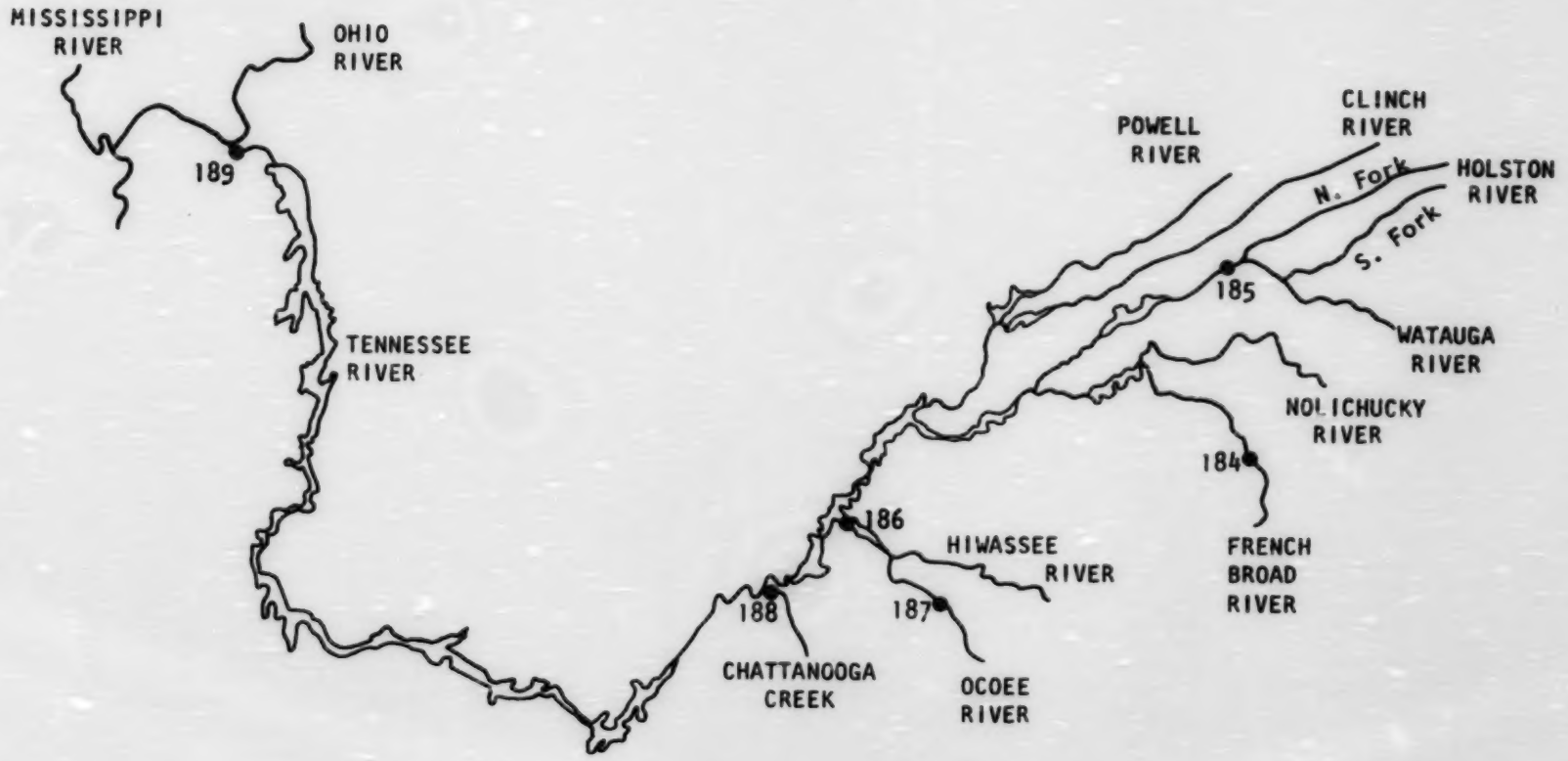


Figure 13. Sites sampled in the Tennessee River basin.

Table 7

Sampling Sites on the West Coast

Sample Number	Waterway	Station	Latitude	Longitude	Nearest Point, River Bridge, or Highway	Nearest Town	Remarks
190	Burbank Western Wash	Glendale	34.09.39	118.18.14	Stanton Ave.	Glendale, CA	Midchannel
191	Los Angeles River	South Gate	33.57.10	118.10.20	Firestone Blvd.	South Gate, CA	Midchannel
192	Los Angeles River	Long Beach	33.46.02	118.12.16	Ocean Blvd.	Long Beach, CA	Midchannel
193	Los Angeles Harbor	Los Angeles	33.45.00	118.16.14	Vincent Thomas Bridge	Los Angeles, CA	Midchannel
194	Dominguez Channel	Carson	33.48.22	118.13.37	Sepulveda Ave.	Carson, CA	Midchannel
195	Ballona Creek	Playa Del Rey	33.58.03	118.19.09	Lincoln Blvd.	Playa Del Rey, CA	Midchannel
196	San Pablo Strait	San Pablo Point	37.59.04	122.25.43	San Pablo Point	San Pablo, CA	"R2"*
197	San Pablo Bay	San Pablo	38.01.47	122.22.19	Point Pinole	San Pablo, CA	"5"*
198	Carquinez Strait	Valona	38.03.38	122.15.41	Davis Point	Valona, CA	"5"*
199	Carquinez Strait	Port Costa	38.02.50	122.10.18	Port Costa	Port Costa, CA	"5"*
200	Willamette River	Portland	45.34.28	122.37.49	SPS RR Bridge	Portland, OR	"5"*
201	Willamette River	Oregon City	45.21.54	122.36.03	Sportscraft Marina	Oregon City, OR	Shore
202	Willamette River	Wheatland Ferry	45.05.06	123.00.55	Wheatland Ferry	Wheatland, OR	Shore
203	Commencement Bay	Tacoma	47.14.18	122.30.58	Commercial Street	Tacoma, WA	Shore
204	Duwamish River	Seattle	47.34.00	122.21.10	Spokane Street	Seattle, WA	Midchannel

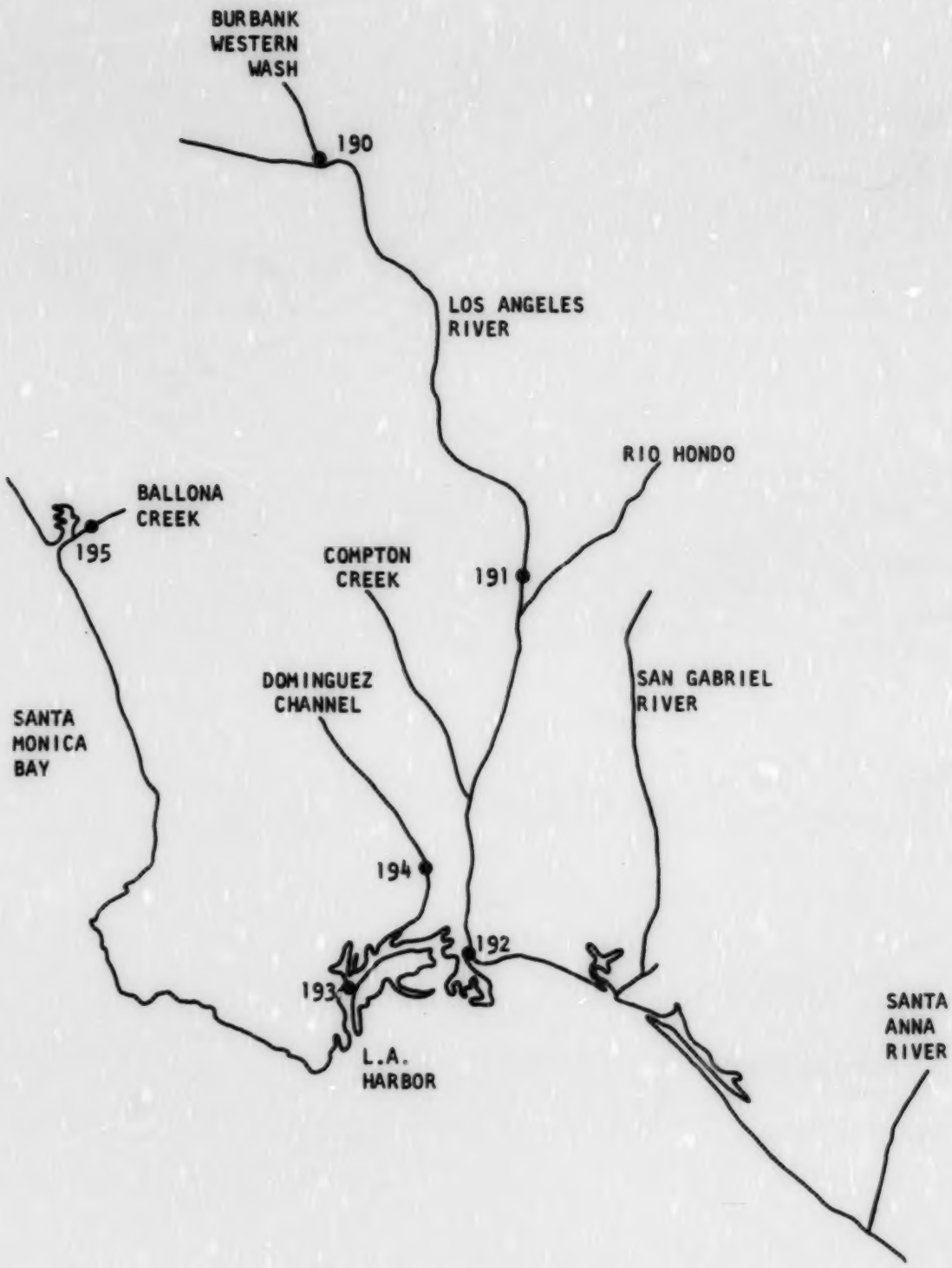


Figure 14. Sites sampled in the Greater Los Angeles area.

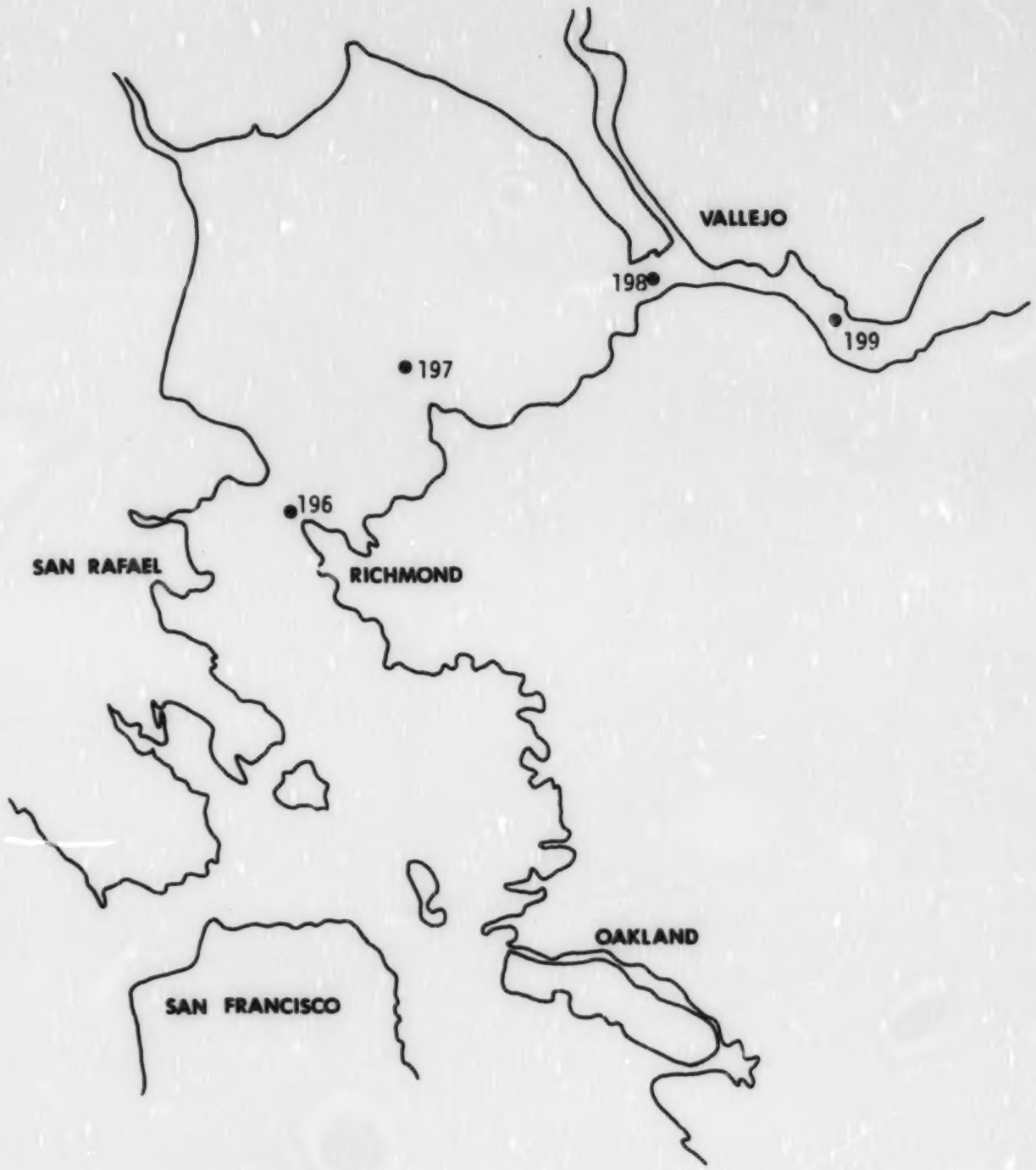


Figure 15. Sites sampled in the San Francisco Bay area.

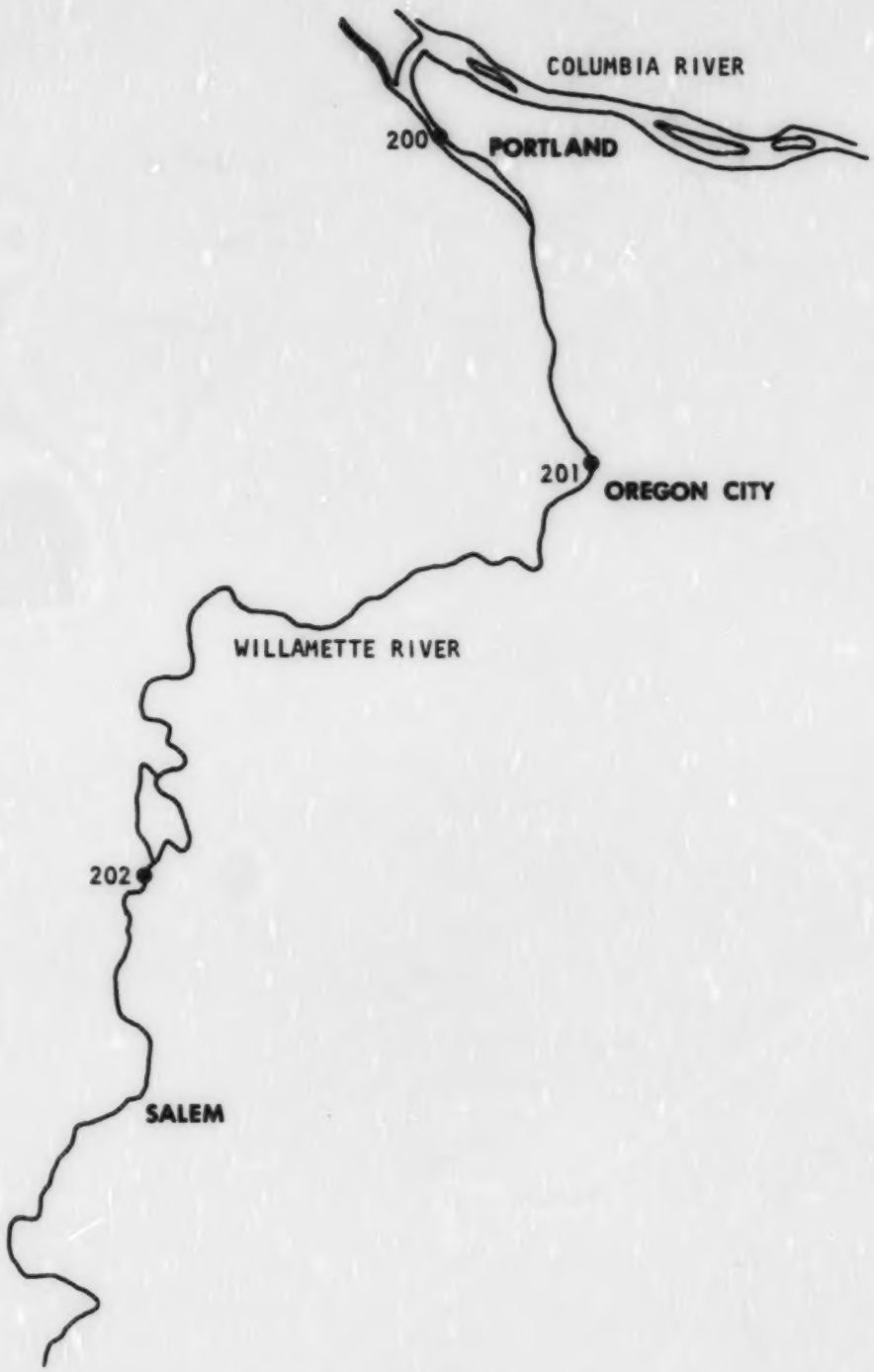


Figure 16. Sites sampled on the Willamette River and in the Greater Portland area.

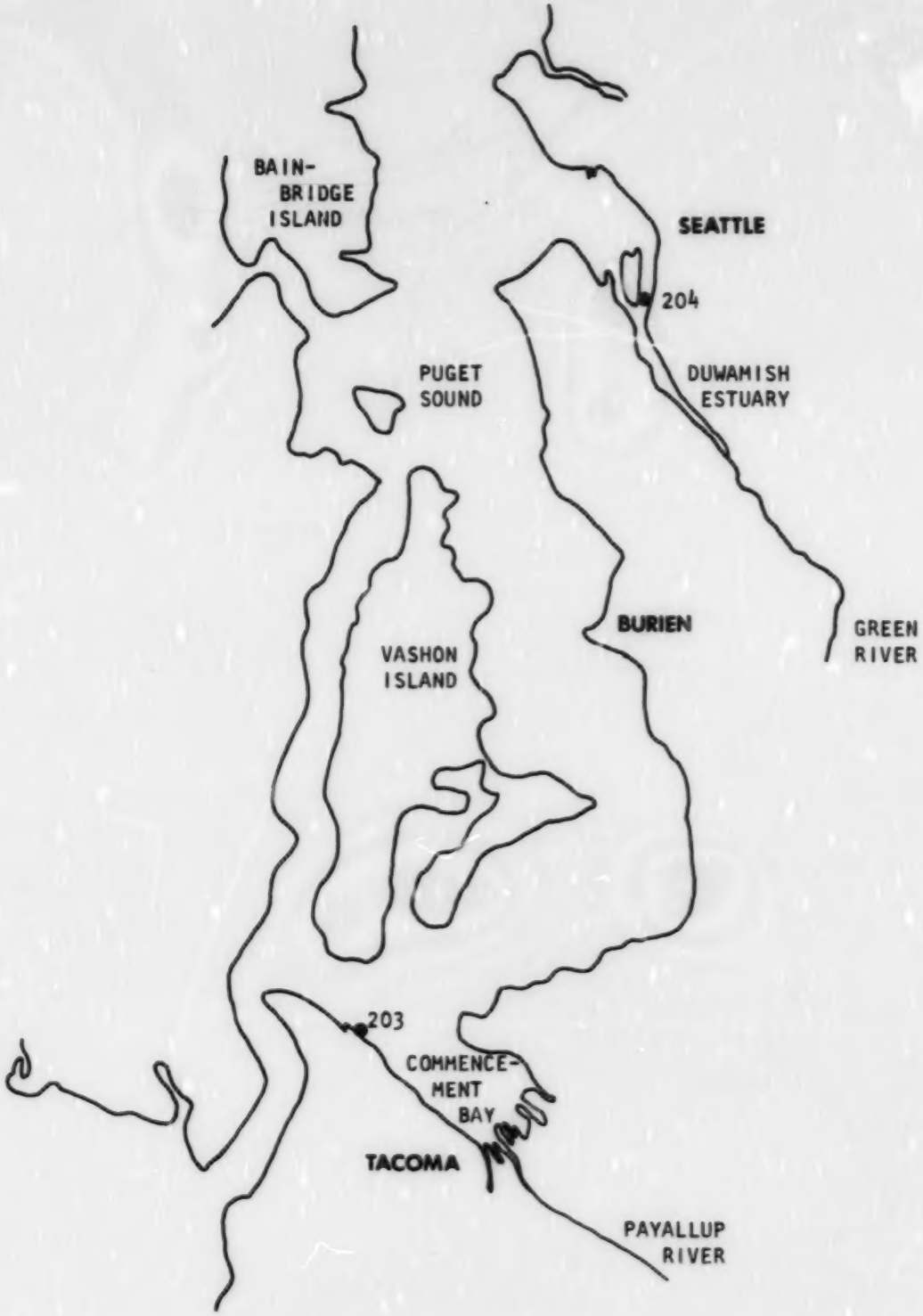


Figure 17. Sites sampled in the Seattle-Tacoma area.

Most of the samples from major rivers and canals were collected in midstream or at the location of greatest river depth. In some instances, shore samples were taken when the established sampling sites were located on the shore instead of in the middle of the waterway. Midstream samples were generally taken from a boat or from bridges and spillways.

The sequence of sampling generally followed the flow of the river. Estuarine samples were generally taken during low slack tide, which at a given location is the time just before the outgoing tide reverses to an incoming tide. No flow occurs in the estuary at that location and time, and collected pollutants therefore generally reflect the discharge at the location. Since the low slack tide starts at the mouth of the estuary and subsequently travels upstream, samples were collected in a corresponding sequence.

SAMPLE COLLECTION

The waterway samples were collected with a 3.8-liter (1-gallon) glass bottle clipped into a metal frame. Depth-integrated samples were obtained by dropping the bottle from a height of 63 centimeters above the surface and allowing it to fall freely through the water. When it reached the bottom, the bottle was pulled up rapidly. During ascent, the remaining air in the bottle expanded and left the bottle, preventing additional water from entering.

Prior to sampling, tests were conducted to study the water inflow rate versus time. The sampling bottle was suspended at two different depths, 1.5 meters and 3.5 meters, and allowed to fill. As Figure 18 shows, the inflow rate is nearly linear with time at both depths. Further experiments were conducted to determine the rate at which such a bottle fills when lowered through the water column. It was found that releasing the bottle at the water surface and allowing it to fall freely through the water resulted in a disproportionately large amount of water entering the bottle in the first meter below the surface. Allowing the bottle to drop from a height of 63 centimeters above the surface, however, minimized this nonlinearity, as shown in Figure 19.

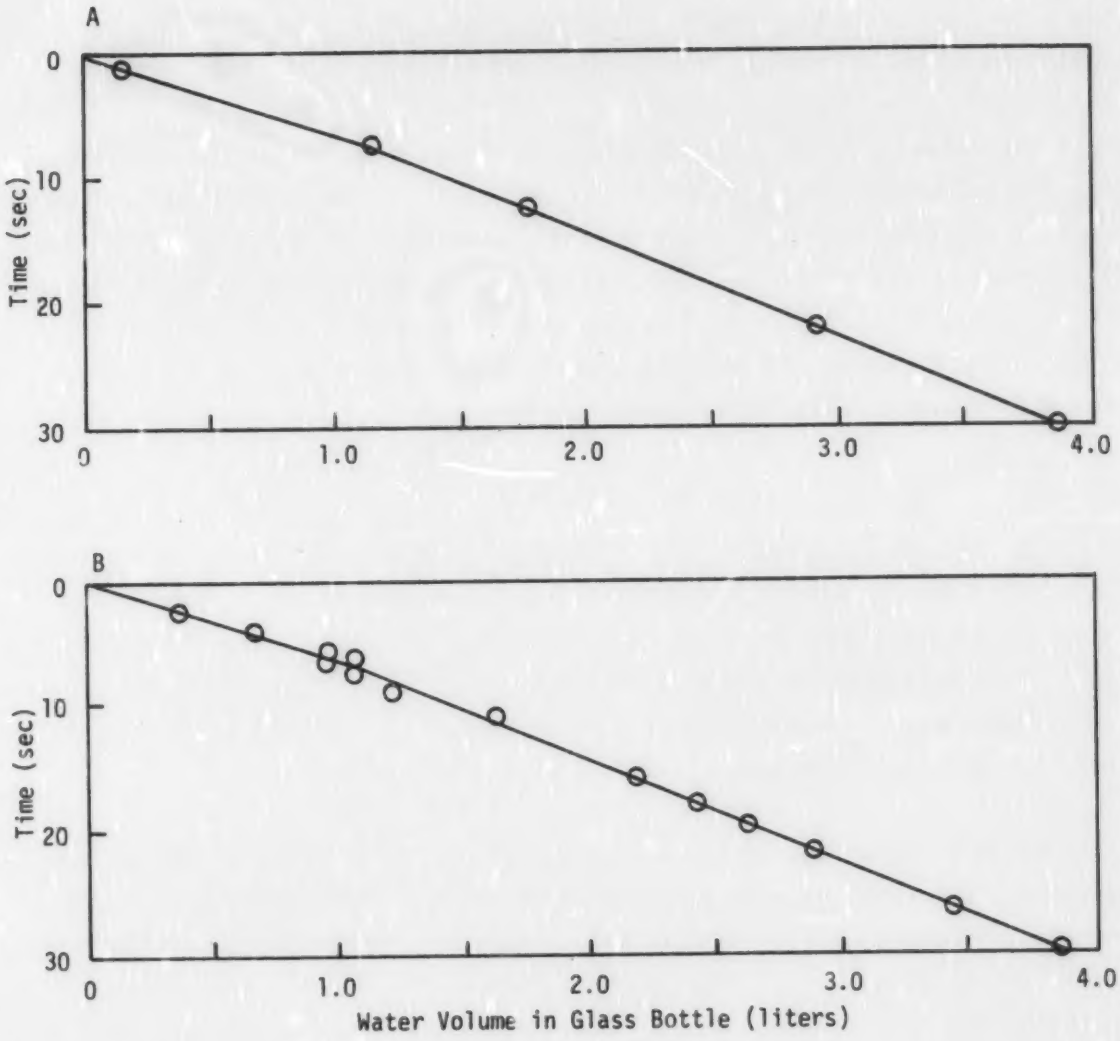


Figure 18. Rate of water inflow into a sample bottle suspended at constant depths of (a) 1.5 m and (b) 3.5 m.

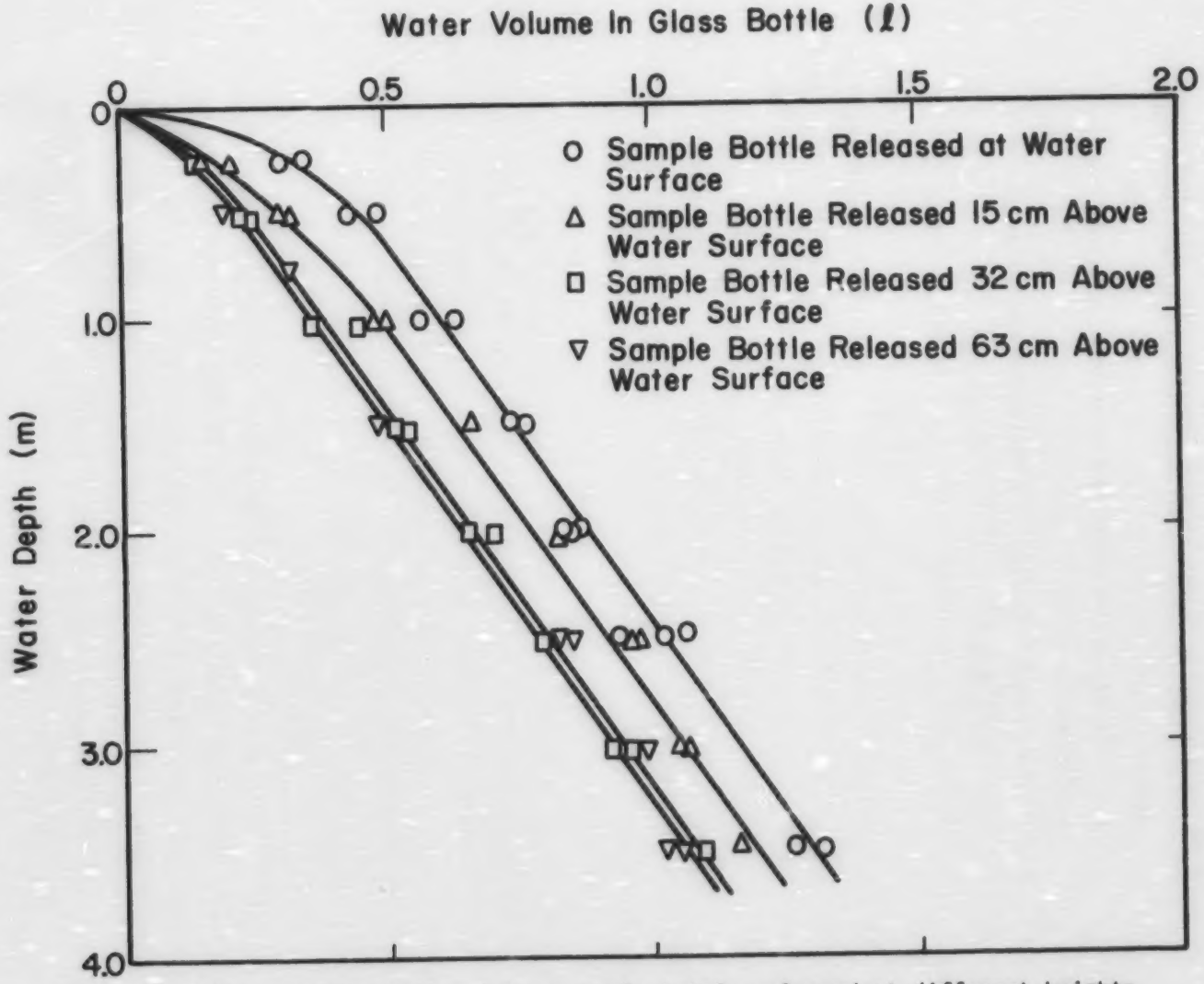


Figure 19. Rate of water inflow into a sample bottle released at different heights above the water surface and allowed to fall freely through the water column.

The sample was divided among eight different storage containers:

1. a 3.8-liter (1-gallon) glass bottle for analysis of extractable organics
2. a 3.8-liter (1-gallon) glass bottle for a reserve sample
3. a 1.9-liter (0.5-gallon) polyethylene container for inorganic analysis
4. a 1.9-liter (0.5-gallon) polyethylene container for gross analysis
5. four 120-ml vials for analysis of volatile organics

Both the sampling bottle and the storage containers were thoroughly cleaned prior to sample collection. The glass bottles were new or baked at 350° C overnight to remove any traces of organics, while the polyethylene containers were rinsed first with nitric acid and then with distilled water to remove any heavy metals which might be attached to the container wall. Immediately prior to filling, the containers were rinsed three times with portions of the sample. The sample was poured into the eight containers in rotation, each being only partially filled at each pass to insure uniform division of the sample. The sampling process was repeated until all storage bottles were filled. The samples for inorganic analysis were stabilized by acidifying them with three ml per liter of ultrapure nitric acid supplied by the U. S. Bureau of Standards. The containers were closed with teflon-lined caps, refrigerated immediately, and transported to the analytical laboratories by surface courier or air freight.

GROSS ANALYSIS

In addition to advanced analyses for trace organic and inorganic contaminants, each sample was subjected to an analysis for gross pollutants for comparison with data collected previously at the same sampling sites. The parameters examined were:

1. total chemical oxygen demand (COD)
2. turbidity

3. conductivity
4. pH
5. color
6. oxidation reduction potential (ORP)
7. suspended solids
8. volatile suspended solids

The results of these analyses have been presented in the quarterly reports. Table 8 gives the location of the results for each sample.

TABLE 8

Location of Gross Analysis Data for All Samples

Sample Number	Report Number	Table Number	Page
1-6	PR 1	2	13
7-31	PR 2	3	10
32-61	PR 3	4	11
62-89	PR 3	5	12
90-134	PR 4	3	12
135-173	PR 5	5	16
174-204	PR 5	6	17

To indicate the range of water quality exhibited by the 204 water samples collected, the results of the gross analyses are summarized in Table 9. Mean values are presented only for the COD and suspended solids measurements because the other parameters are not linear functions of concentration and mean values would therefore have no significance.

Table 9
Summary of Gross Analysis Data

Parameter	Minimum	Mean	Maximum
pH	5.21		9.80
Turbidity, JTU	0.1		92.5
Total COD, mg/l	1.3	33.0	78.5
Suspended Solids, mg/l	0	31.1	194
Color (absorbance at 400 nm)	.000		.690
ORP, +mv	100		458

The lowest COD was encountered in the Delaware River at Torresdale and the highest at Burbank Western Wash near Glendale, California. The suspended solids concentration was lowest in the Hudson River at Corinth and highest in the Mississippi River at New Orleans. Turbidity, on the other hand, was lowest in the water flowing out of Lake Superior through St. Mary's River and highest in the Houston Ship Channel near Shaver Road. Color was maximum in the Wisconsin River at Nekoosa, Wisconsin. The pH varied from 5.21 in the Hudson River at Bayonne, N.J., to 9.80 in the Saginaw River at Bay City, Michigan. The ORP was minimum in the Ohio River at the Belleville Lock and Dam and maximum at the mouth of the Schuylkill River at Philadelphia.

3. SAMPLE PREPARATION

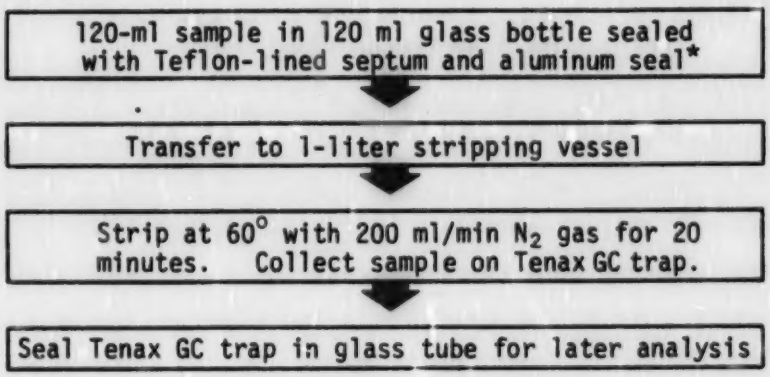
E. S. K. Chian
J. H. Kim

Samples to be analyzed for volatile organic contaminants were prepared by a stripping procedure; those for the less-volatile organics were prepared by liquid-liquid extraction techniques. They were then forwarded to the laboratories which performed the quantification and identification procedures described in Chapter 5.

STRIPPING PROCEDURES

The volatile organic compounds were stripped from the incoming samples by a technique similar to that described by Chian and Kuo (1975) and illustrated in Figure 20. The compounds were stripped from a 120-ml sample at a temperature of 60° C by passing nitrogen through the sample at a rate of 200 ml per minute. The compounds were adsorbed in a Tenax GC trap, which was then sealed in a glass tube and transmitted to the appropriate laboratories for analysis. All glassware was baked at 450° C overnight prior to use. The stripping efficiency of this method was in the range from 12 to 100 percent, depending on the initial concentrations and the physical properties of the compounds present.

The stripping procedure of Bellar and Lichtenberg (1974) was used initially for this project, the sample being held at 98° C during the stripping operation. It was found, however, that at that temperature excessive moisture accumulated in the Tenax traps, interfering with later analysis by gas chromatography-mass spectrometry (GC/MS). Stripping tests conducted at various temperatures indicated that the moisture content in the trap decreased with temperature. Below 65° C, however, the stripping efficiency for compounds with a relatively high boiling point and those that are less polar (such as hexane and toluene) decreased appreciably. Recovery of polar compounds was optimum at about 65° C. The temperature ultimately selected, 60° C, represented the best compromise between these variables. Problems with background contamination from the Tenax traps and from the Carbowax 1500 GC columns provided another impetus for changing


120-ml sample in 120 ml glass bottle sealed with Teflon-lined septum and aluminum seal*
Transfer to 1-liter stripping vessel
Strip at 60° with 200 ml/min N_2 gas for 20 minutes. Collect sample on Tenax GC trap.
Seal Tenax GC trap in glass tube for later analysis

*Kopfler *et al.*, 1976

Figure 20. Procedure for stripping volatile organic compounds.

the stripping procedure. Initially, the volume of sample stripped was 5 ml. Increasing it to 125 ml made it possible to exceed the background contamination level by a significantly greater margin. The level of background contamination from the stripping flask, Carbowax 1500 GC column, and the Tenax traps was measured at less than the 0.03 ppb level.

A number of other tests of the stripping procedure were also conducted using prepared samples containing selected concentrations of 12 model compounds. Specifically, the following parameters were examined:

1. techniques for transferring the samples from the storage bottles to the stripping flask
2. reproducibility of the stripping procedure
3. variation in stripping efficiency (recovery rate) with stripping gas flow rate
4. variation in stripping efficiency with stripping time
5. variation in stripping efficiency with stripping flask size
6. variation in stripping efficiency with the concentration of compounds in the original sample
7. the effects of storing the Tenax traps for periods of 5 and 28 days in sealed glass tubes after stripping

The results, presented in Progress Report Number 3, were used in establishing the stripping procedure ultimately adopted.

LIQUID-LIQUID EXTRACTION

The less-volatile organic compounds were extracted from the water samples using the procedure shown in Figure 21. Each sample was first spiked with camphor, which served as an internal standard. The pH was adjusted to approximately 12, and the sample was extracted using nanograde chloroform. The solvent

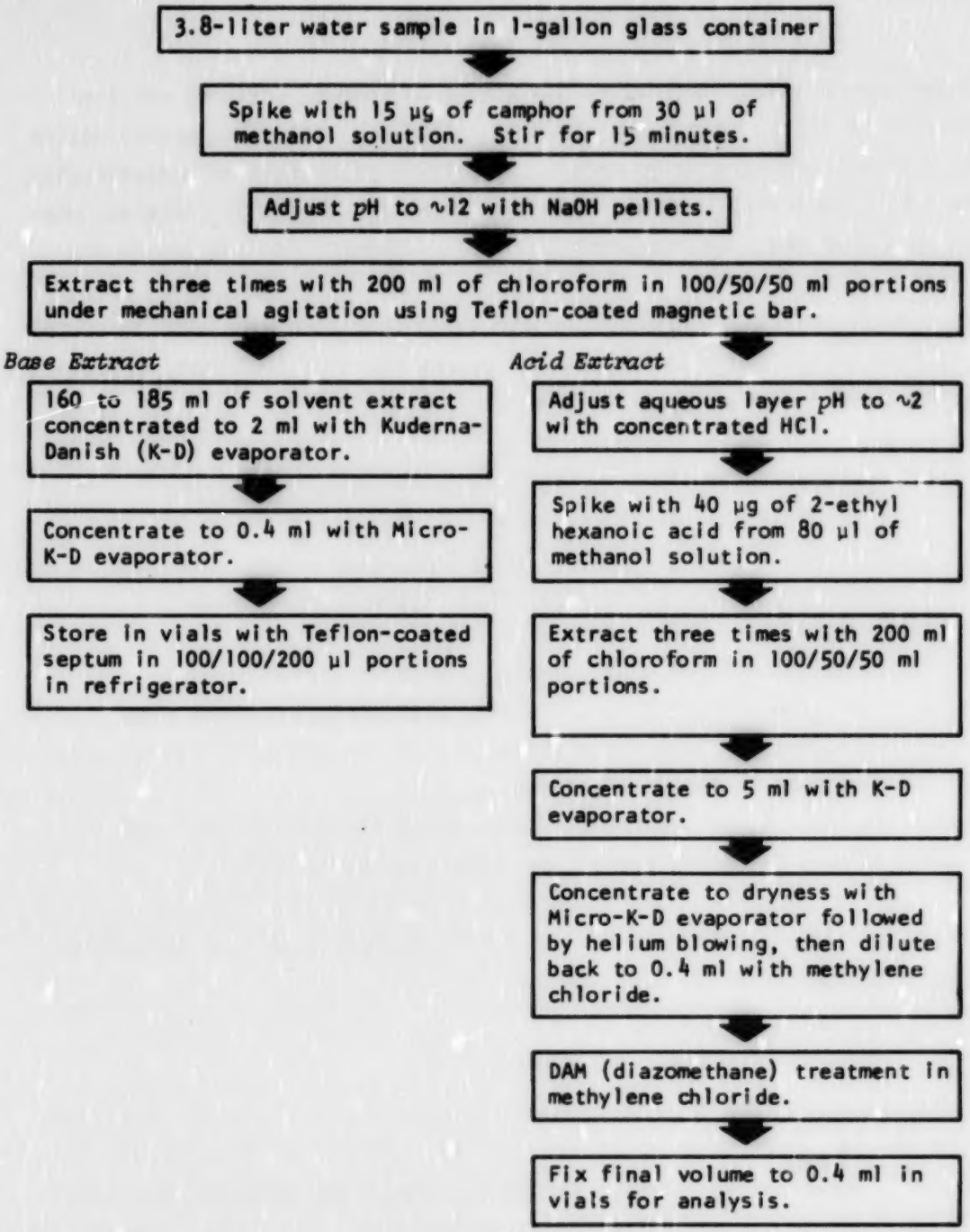

3.8-liter water sample in 1-gallon glass container
Spike with 15 µg of camphor from 30 µl of methanol solution. Stir for 15 minutes.
Adjust pH to ∿12 with NaOH pellets.
Extract three times with 200 ml of chloroform in 100/50/50 ml portions under mechanical agitation using Teflon-coated magnetic bar.
Base Extract
160 to 185 ml of solvent extract concentrated to 2 ml with Kuderna-Danish (K-D) evaporator.
Concentrate to 0.4 ml with Micro-K-D evaporator.
Store in vials with Teflon-coated septum in 100/100/200 µl portions in refrigerator.
Acid Extract
Adjust aqueous layer pH to ∿2 with concentrated HCl.
Spike with 40 µg of 2-ethyl hexanoic acid from 80 µl of methanol solution.
Extract three times with 200 ml of chloroform in 100/50/50 ml portions.
Concentrate to 5 ml with K-D evaporator.
Concentrate to dryness with Micro-K-D evaporator followed by helium blowing, then dilute back to 0.4 ml with methylene chloride.
DAM (diazomethane) treatment in methylene chloride.
Fix final volume to 0.4 ml in vials for analysis.

Figure 21. Procedure for extraction of the less-volatile organics.

and aqueous layers were then separated. The solvent was concentrated to 0.4 ml in evaporators, and the resulting base extract was stored in three vials, one containing 200 µl and two containing 100 µl each. The latter two vials were transferred to the appropriate laboratories for analysis.

The remaining aqueous layer was then adjusted to a pH of between 2 and 3 and spiked with 2-ethyl hexanoic acid as an internal standard. It was extracted with chloroform and the solvent was concentrated to 5 ml in an evaporator. The chloroform was then exchanged with a different solvent, methylene chloride, by evaporating the sample to dryness and then diluting it to a 0.4-ml volume with the latter compound. The resulting acid extract was methylated with diazomethane. The final volume was adjusted to 0.4 ml and the sample was transmitted to the analytical laboratories in the same volumes as for the base extracts.

In the process used initially for preparing the acid extracts, the chloroform was not exchanged with methylene chloride. A high level of sample contamination was observed, however. Because the level of impurities in the nanograde chloroform used was found to be less than 0.01 ppb, the contamination of the sample was attributed to impurities in the diazomethane used as a methylating agent. Further tests revealed that the interfering contaminants were not present in the diazomethane but were formed as side-reaction products between the diazomethane and the chloroform solvent. This problem did not arise when methylene chloride was used as the solvent. The recovery of organic compounds was better when the sample was extracted with chloroform, however. Therefore, chloroform was used for the initial extraction but replaced with methylene chloride prior to the methylation step.

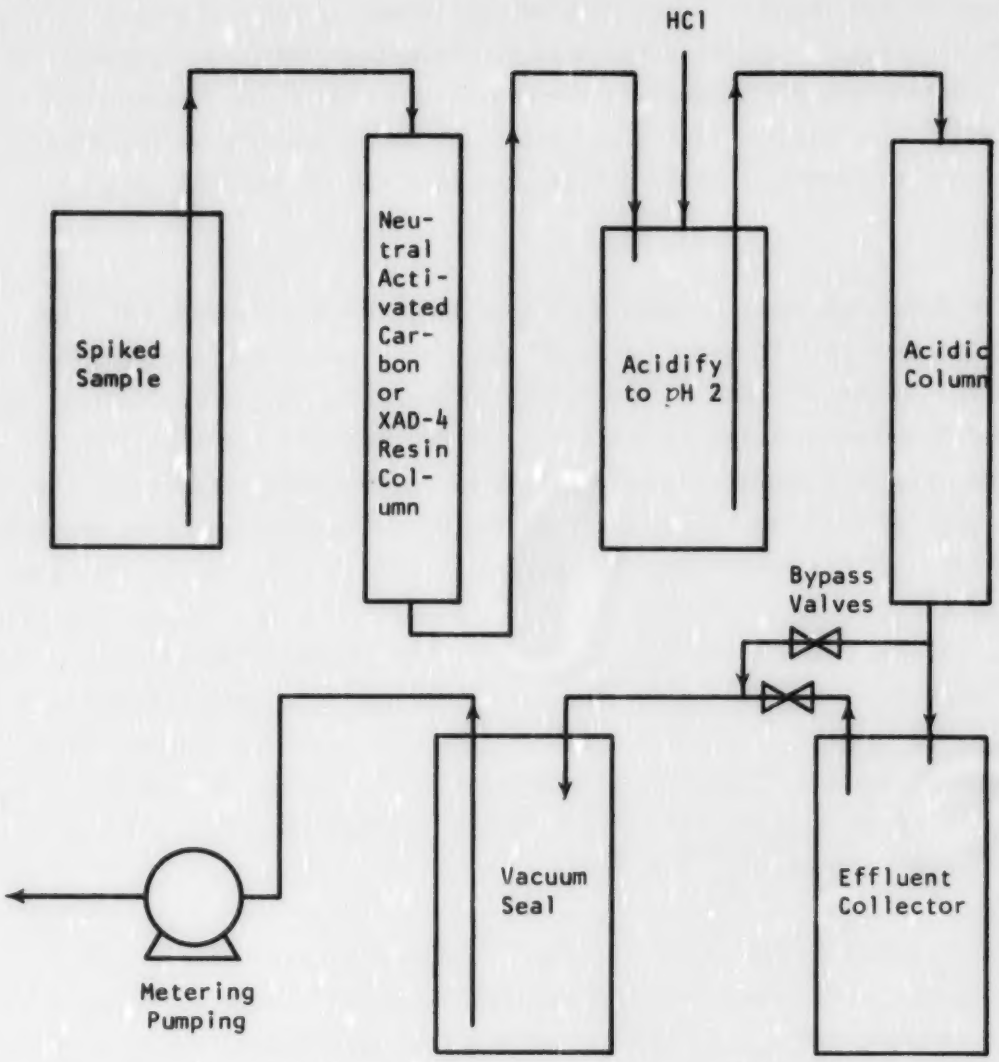
SORPTIVE EXTRACTION TECHNIQUE

Adsorption onto a sorptive medium was evaluated as a possible alternative to the liquid-liquid extraction process for preconcentrating the less-volatile organic compounds. XAD-4 resin (Rohm and Haas, Philadelphia, Pennsylvania) and six types of activated charcoal were evaluated for their effectiveness as sorptive media. Of these, the XAD-4 resin and Widco activated carbon (Widco Chemical Corp, N.Y.) exhibited the lowest levels of background contamination and were therefore chosen for further testing.

Samples number 18 and 19 were used to compare the effectiveness of the sorptive technique with the liquid-liquid extraction method. These samples were processed both by the normal procedure in the laboratory and by the sorptive method at the sample collection site using the experimental setup shown in Figure 22. Several different methods for processing the resulting resin and carbon samples were evaluated. The analytical procedures applied to sample 18 were described in Progress Report Number 2. Based on the results, the process was modified somewhat for sample number 19, as described in Progress Report Number 4.

The activated carbon was found to be better for sampling neutral organics than was the XAD-4 resin, as indicated by the number of peaks observed. For acidic organics, the number of peaks for the two sorptive materials were comparable, but the carbon column exhibited some impurities.

The data indicate that preconcentration by the use of sorptive materials in columns is superior to liquid-liquid extraction for neutral organic compounds, while the two methods produce comparable results for acidic organics.



Amount of Sample Used:	200 liters
Spiking Compound and Amount:	0.253 mg of camphor and 1.51 mg of 2-ethyl hexanoic acid dissolved in 3.5 mg CH_3OH per 200-liter sample
Flow Rate:	~60 ml/min
Period of Experiment:	4 to 5 days

Figure 22. Flow diagram of experimental setup for sorptive studies.

4. INORGANIC ANALYSIS

Inorganic multielemental analysis was performed by three separate and independent techniques: spark-source mass spectrometry (SSMS), instrumental neutron activation analysis (INAA), and energy-dispersive x-ray fluorescence (XRF) analysis. The results of the analyses have been presented in the five quarterly progress reports. Table 10 lists the location of the SSMS data for all samples.

The SSMS technique is capable of detecting or establishing detection limits for approximately 80 elements in the type of water sample analyzed for this project. For 44 of these elements the semiquantitative determination is confirmed by either a multiply charged or second isotopic spectral line. For the remaining 36 elements the analysis is based on a single spectral line. For 22 of those 36 elements the INAA and XRF methods are able either to provide a quantitative confirmation of the SSMS estimates (for Sc, Co, Ni, Se, Sb, and Hg) or to establish a better detection limit than SSMS (for Mo, Ru, Ag, Cd, Cs, Ce, Sm, Eu, Tb, Yb, La, Hf, Ta, Re, Ir, and U). The combined use of these techniques provided two significant benefits. The number of unconfirmed analyses was reduced from 36 to 14, and confirmed analyses were obtained on six of the seven environmentally important elements: Pb, Tl, Cd, Hg, Se, and As. (Three were confirmed by INAA and three by XRF). Only the Be determination depended on a single analytical technique.

The analyses by the three different techniques agreed within the limits of detection and experimental error for almost all elements. INAA determinations (44 elements) are quantitative within the stated limits, as are the XRF determinations. SSMS determinations are semiquantitative; the true concentration is expected to be within the range from one-third to three times the stated value. SSMS values obtained for the alkali metals and alkaline-earth metals appear to be somewhat higher than the INAA and XRF results.

It can be concluded that the three complementary techniques yield a complete elemental analysis of this type of water sample. Limitations associated with one method are usually compensated by high sensitivities of the other methods.

Table 10

Directory of Inorganic Analyses

Sample Number	Progress Report Number		
	SSMS	INAA	XRF
1 - 6	PR1	PR1	PR1
7	PR2	PR2	PR2
8, 9	PR2	PR5†	PR2,5*
10, 11	PR2	PR2	PR2
12	PR2	PR5†	PR2,5
13	PR2	PR2	PR2
14	PR2	PR5	PR2,5
15 - 17	PR2	PR2	PR2
18 - 31	PR2	PR5†	PR2,5
32 - 38	PR3	PR5	PR3,5
39 - 41	PR3	PR4	PR3,4
42	PR3	PR5	PR3,5
43	PR3	PR5	PR5
44 - 46	PR3	PR5	PR3,5
47	PR3	PR4	PR3,4
48, 49	PR3	PR5	PR3,5
50 - 61	PR3	PR4	PR3,4
62 - 73	PR3	PR5	PR3,5
74 - 84	PR3	PR4	PR3,4
85, 86	PR3	PR5	PR3,5
87 - 89	PR4	PR5	PR3,5
90 - 102	PR4	PR4	PR4
103, 104	PR4	PR5	PR5
105 - 107	PR4	PR4	PR4
108 - 110	PR4	PR5	PR5
111 - 117	PR4	PR4	PR4
118 - 120	PR4	PR5	PR5
121 - 134	PR4	PR4	PR4
135 - 204	PR5	PR5	PR5

*Where two progress report numbers are listed, complete XRF data are presented in both reports.

†Partial INAA results for these samples were presented in Progress Report No. 2; the complete data were presented in Progress Report No. 5

SPARK-SOURCE MASS SPECTRAL ANALYSIS

C. A. Evans
W. H. Wadlin

Most of the samples analyzed by SSMS were composited, consisting of from two to five individual samples. Samples analyzed as composites were grouped according to geographic origin and expected composition. For example, composite XXIII comprised three consecutive samples which represent the upper Hudson River, and composite LXV comprised waters from three tributaries to Lake Erie. Of the eighty composites, fourteen consisted of only one component sample. Also, the first six samples were analyzed individually and were not assigned composite numbers. In addition to these 86 samples which constitute the reported SSMS results, an additional 62 samples consisting of standards, blanks, replicates, and research samples were processed during the course of the project.

Procedure

The samples were evaporated in the presence of a suitable matrix material and the residues formed into electrodes. A laboratory study indicated that the loss of trace elements by volatilization during the bulk evaporation process was insignificant when a silver matrix was used. A total volume of 100 ml of sample per composite was nominally used. There was no advantage to using more sample, since the detection limits for most elements were limited by the appearance of organic interferences in the spectra. Thus, detection limits become lower as the sample size is increased up to the point at which the electrodes are so heavily loaded with sample that enough organics are present to appear in the longest exposures, interfering with element identification. For saltwater samples, only 25 ml could be used because of interferences from inorganic molecular ions. The samples were doped with 50 µg of yttrium as an internal standard and evaporated nearly to dryness in Pyrex evaporating dishes with 1.0 g of matrix material at 80°C. The drying was completed in an oven at 105°C. Silver powder was used as the matrix material in preference to graphite, as it resulted in fewer matrix interferences and higher sensitivity. The residue was then transferred to a plastic ball mill for mixing. Since the dried residues

were frequently quite hygroscopic, it was found necessary to make the transfer quickly while the material was still warm and to store it immediately in a dessicator. After mixing, the powder was pressed into electrodes in a polyethylene slug.

The electrodes were mounted in the AEI MS-7 mass spectrometer for analysis using photographic detection. The samples were presparked for the equivalent of a 30 nC exposure at 30 pulses per second. This process removed surface contamination and the abnormally high initial sensitivity caused by the adsorption of trace elements contained in the sample on the surface of matrix particles. Although it was considered possible that some elements could be lost by thermal vaporization from the electrodes during the sparking process, tests conducted using a sample containing model elements indicated that selective volatilization was not a problem.

In obtaining the analytical exposures the pulse repetition rate was kept as low as was practical for obtaining the exposure in a reasonable amount of time. The maximum pulse repetition rate used was 100 pulses per second regardless of the time required to obtain the exposure. Higher rates caused sufficient heating of the electrode bulk to drive organic materials out from the interior, giving rise to severe interferences and unacceptably high detection limits. Three exposures per decade of exposure magnitude were obtained over the range from .001 to 300 nC.

Concentrations of trace elements were determined by comparing the exposures required for their spectral lines to be just detectable with the equivalent exposure for the internal standard. Elemental sensitivities were assumed to be equal. The results were presented in the appendices of the five quarterly progress reports. If an element was confirmed by the presence of either a multiply charged ion or multiple isotopes of the correct relative intensities, the value for that element was given without a prefix symbol. If the value was prefixed by the symbol "<" (meaning "less than or equal to") it indicates that a line corresponding to the +1 ion of that element was observed, but its presence could not be confirmed by the procedures above.

That is, either the element was present at the concentration stated or there was an interference. The symbol "*<" (meaning "definitely less than") was applied if no lines were observed which could be attributed to this element or if there was a definite, known interference. In cases where no line was observed, the number given was calculated on the basis of what the concentration would be had the element been just detectable in the longest exposure. In the case of a known interference, the value given was the concentration at which the element would have had to be present to appear with an intensity equal to that observed for the interference.

Discussion of Results

Considering that the data were taken with three exposures per decade and that there are some differences in elemental sensitivity, the results reported should generally be accurate to within one-third to three times the actual concentration. Detection limits are generally in the range from 0.2 to 2 µg/l for freshwater samples. For saltwater samples, inorganic molecular interferences and a general loss of sensitivity raise the detection limits to the range from 20 to 200 µg/l.

Comparison of SSMS results with the INAA and XRF results for these samples shows general agreement within the expected range of errors given above. Notable exceptions are the concentrations determined for K, Mg, and Ca. The SSMS results for K and Mg are consistently higher by about a factor of 3 and for Ca are higher by a factor of 5 to 10. Analysis of standards indicates that the error is in the SSMS determination and results from unusually large differences in sensitivity for these elements, a factor not compensated for in the calculations.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

P. K. Hopke
J. D. Sherwood

Procedure

The sensitivity of instrumental neutron activation analysis (INAA) is governed by the number of neutrons with which a sample is irradiated, the delay time between irradiation and the start of the count, and the counting time

intervals. Other investigators (Clemente and Mastinu, 1974; Salbu *et al.*, 1975) have used various methods of applying INAA to obtain determinations of trace elements in water samples. In some studies where a small number of samples were processed, long irradiation intervals (up to 72 hours) were used. For the large number of samples involved in the present project, however, long intervals become economically unfeasible because of reactor costs. Therefore, a relatively short interval was used, compensated for by using larger sample volumes, counting the irradiated samples for comparatively longer intervals, and using a more efficient gamma counting system. The following procedures were used for freshwater and saltwater samples through number 94.

Freshwater Samples

1. The quartz ampoules used to hold the samples during irradiation were pretreated in a bath of dilute nitric acid at 85°C for four hours to remove any contaminants
2. A 15-ml sample was loaded into each ampoule, which was then heat-sealed
3. The sealed ampoules were tested to insure that they would not break from thermal stress during irradiation
4. The samples were irradiated for 30 minutes at 500 kW
5. After a decay period of three days, the samples were transferred to standard polyethylene counting vials. The ampoules were rinsed with two 1-ml portions of dilute hydrochloric acid to recover any adsorbed molecular or ionic species and the rinse was added to the contents of the counting vial
6. The emitted radiation was counted for 1,000 seconds using a 10% Ge(Li) detector in conjunction with a 4096-channel analyzer system
7. The samples were repackaged and irradiated for eight hours at 1.5 MW
8. After a decay period of 14 days, the samples were transferred to counting vials as before and the emitted radiation was counted for 4,000 seconds

Saltwater Samples

1. The ampoules were pretreated as for freshwater samples
2. Each ampoule was loaded with a 10-ml sample and heat-sealed
3. The ampoules were tested for thermal stress resistance
4. The samples were irradiated for eight hours at 1.5 MW
5. After a decay period of seven to ten days the samples and acid rinse were transferred to polyethylene counting vials
6. The emitted radiation was counted for 1,000 seconds
7. After an additional 7-day decay period, the sample radiation was counted for 20,000 seconds

Data obtained from the multichannel analyzer system were transferred to magnetic tape for computerized peak analysis. Two computer programs were written which combine peak identification and quantitative calculations in a single computer run. The results have been presented in the five quarterly reports. Table 10 lists the location of INAA data for all samples.

A preconcentration procedure was adopted for freshwater samples above number 94 in order to achieve a higher rate of sample analysis. Preconcentration permits the use of larger sample volumes with a proportionate decrease in the required counting time. The samples were preconcentrated by evaporation in the presence of AVICEL, a microcrystalline cellulose, which acts as an adsorption medium for the inorganic constituents. A 500-ml sample is evaporated with 100 mg of AVICEL at 50°C in a polyethylene beaker and quantitatively transferred to an irradiation container. In addition to faster sample analysis, this technique provides lower detection limits and reduces the hazards of handling the samples after irradiation. The disadvantages are the increased possibilities of contamination and errors resulting from loss of sample during the transfer.

ENERGY-DISPERSIVE X-RAY FLUORESCENCE ANALYSIS

P. K. Hopke
J. D. Sherwood

Samples analyzed by energy-dispersive x-ray fluorescence were preconcentrated by three methods:

1. Precipitation with ammonium-1-pyrrolidine dithiocarbomate (APDC) at a pH of 4 and filtration through a 25-mm 0.2 μ-pore Nuclepore filter
2. Precipitation of cyanide complexes at a pH of 12.0 followed by filtration twice through Reeve Angel SB-2 anion-exchange paper
3. Filtration twice through Reeve Angel SA-2 cation-exchange filter paper at a pH of 2.0

Each sample was divided into two aliquots, each of which was analyzed separately. For samples through number 89, one sample was preconcentrated by the first (APDC) method while the other portion was preconcentrated by one of the other two methods. For later samples, both portions were preconcentrated by the APDC technique, since it was found to yield the most consistent recovery rate for the elements analyzed in both freshwater and saltwater samples.

The basic procedure used for analyzing samples by the XRF method was as follows:

1. A 1% w/v APDC solution was prepared daily and filtered through a 0.2 μ Nuclepore filter.
2. The water sample was shaken sufficiently to resuspend particulate matter.
3. Two 50-ml aliquots were removed and the pH was adjusted to 4.0.
4. 5 ml of APDC solution was added and the precipitation process was allowed to develop for approximately 15 minutes.

5. The precipitate was filtered through a 25-mm, 0.2 μ Nuclepore filter.
6. After the filter dried, it was mounted between 0.00010-in. Mylar film on a polyethylene XRF sample cup.
7. The sample was positioned under the source exciter system.
8. Each sample was counted for 10^4 seconds for each secondary target (Mo and Dy).
9. The accumulated spectrum was transferred to magnetic tape for processing.
10. Treating the filter as a thin sample, the results were calculated by a method identical to that used by Bonner, Bazan, and Camp (1975), except that all of the material was assumed to be on the top of the filter. With the Nuclepore filters used in this study it is believed that there was very little penetration of precipitate into the filter.

To determine the net area of each peak in the spectra produced, it was necessary to subtract the background level from the region of interest. For the early samples through number 89, a background-stripping computer program similar to that of Bonner, Bazan, and Camp (1975) was used. Discrepancies between the results of XRF analyses and those obtained by the INAA and SSMS techniques were traced to problems with this program. Consequently, for samples after number 89, the background was subtracted manually, resulting in much greater consistency between the three techniques.

The results of the XRF analyses have been presented in the quarterly reports. The location of the XRF data for all samples is listed in Table 10.

5. ORGANIC ANALYSIS

Samples prepared for the determination of organic constituents were divided and sent to two separate laboratories for analysis. For extractable organics, one 100-µl aliquot was sent to the gas chromatography-mass spectrometry (GC/MS) laboratory in the Department of Chemistry for the identification of constituents, and another 100-µl aliquot was analyzed by gas chromatography (GC) in the Department of Food Science to establish the quantity of each contaminant present. Similarly, separate Tenax traps were prepared and sent to the two laboratories for the analysis of volatile organics. Identical gas chromatographic operating parameters were used in the two laboratories, making it possible to use the relative retention times for each compound to correlate the identification and quantification of each peak observed.

In some samples a comparatively large number of compounds were detected at levels below 1 ppb. Because identifying and quantifying all of these compounds would have been excessively time consuming, it was determined in consultation with the sponsor that only those organic substances present at or above the 1 ppb level would be reported.

Preliminary results of the organic analyses were presented in the quarterly reports. Upon completion of sample analysis, the data were reexamined and corrected or adjusted as necessary. The final results are presented in the appendix of this report. In particular, the quantitations were revised on the basis of the relative GC response factors determined for selected compounds, with the result that some compounds formerly determined to be present at concentrations below 1 ppb are now known to be at a higher level and are therefore included in the updated listings. Conversely, some compounds previously listed have been found to be present at concentrations less than 1 ppb and have hence been deleted. In addition, the relative retention times have been rechecked, resulting in corrections to some of the identifications. Compounds which could not be identified were not listed in the previous reports, but their presence is indicated in the final results presented here.

IDENTIFICATION OF ORGANICS

J. C. Cook, Jr.
R. M. Milberg

All of the samples processed by the organic identification laboratory were analyzed on a Varian-MAT 311A combined gas chromatagraph-mass spectrometer with a Varian-Aerograph 2700 gas chromatagraph using a 2-stage Watson-Biemann sample enricher. The system is of all-glass construction from column inlet to source inlet.

Procedures

The Tenax traps for analysis of volatile organic compounds were received from the sample preparation laboratory in sealed glass tubes. The traps were removed from the tubes, connected to the gas chromatagraph, and flushed for two minutes at ambient temperature with helium gas. A tubular furnace with an interior temperature of 250°C was then slipped over the trap and allowed to preheat the trap for two minutes, after which the volatiles were flushed from the trap onto the GC column for four minutes with a helium flow rate of 40 ml per minute. The column was held at ambient temperature during this period. The outside diameter of the glass column used was 6 mm, the inside diameter was 2 mm, and the length was 12 ft. The column was packed with 0.2% Carbowax 1500 on 60/80-mesh Carbopack C (Supelco, Inc., Bellefonte, Pa.). After the volatiles were flushed onto the column, the temperature of the column was programmed to increase at a rate of 8°C per minute from 30°C to 200°C. It was held at the latter temperature for the remainder of the run.

For the analysis of base and acid extracts, 1 µl of the sample was injected onto a glass column of the same dimensions as above but packed with 3% OV-17 on 80/100-mesh Gas Chrom-Q (Applied Science, State College, Pa.). The column temperature was held at 50°C during injection and was then programmed to increase to 300°C at a rate of 8°C per minute.

The mass spectrometer was scanned continuously from an m/e of 33 to an m/e of 350 for volatiles and from m/e 33 to m/e 600 for extractable organics. The scan rate was 2.3 seconds per mass decade, and the ionization potential was

70 eV. Data were acquired on a Varian-MAT SS100 data system and stored on a disk cartridge.

Identification

Mass spectra were identified by inspection, manual searches, and computer searches using the ADP-Cyphernetics Mass Spectral Search System (MSSS). The usefulness of the MSSS was limited by the fact that the spectra for many compounds found in the samples were not in the computer file, nor were there any compounds of similar type. Also, spectra for most of the compounds in the file were obtained by direct-probe mass spectrometry under ideal conditions with the result that many of the spectra were different from those obtained by the GC/MS technique at the 1 ppb level.

The volatile compounds were the easiest to identify because of their low molecular weights and simple spectra and because many of them were halogenated, giving excellent isotope cluster patterns. Compounds in the acid extracts were the most difficult to identify because of the large number of peaks and the fact that the methyl ester spectra for many of the compounds were not present in the MSSS file.

A computer program was developed to calculate the relative retention times of the observed peaks. These relative retention times provided a second confirmation of the identifications and, as discussed above, were used to correlate the identifications of the compounds with their quantitations.

Results

All compounds identified in the samples were listed along with their relative retention times in the quarterly reports. The final adjusted data for those compounds present at concentrations of 1 ppb or greater are presented in appendix B of this report.

QUANTITATION OF ORGANICS

E. G. Perkins
J. C. Means

The work of the quantitation laboratory focused on several areas: (1) quantitative analysis of the stripped volatile, acid extractable, and base extractable organic compounds contained in the 204 surface water samples collected, (2) the optimization of the chromatographic conditions used to separate the organic constituents of each sample fraction, (3) the investigation of conditions affecting the purity of blanks, (4) the investigation of parameters related to the selection of internal standards for the acid and base extractable fractions, and (5) the investigation of parameters related to the separation and quantition of selected amines.

Quantitative Analysis of Purgeable and Extractable Organics

As mentioned previously, the gas chromatographic conditions used in the quantitation laboratory and in the identification laboratory were coordinated during all stages of the project. Initially, base and acid extract samples were run routinely on a Hewlett-Packard 5830A programmable gas chromatograph. One-microliter samples were injected onto a 12-foot by 1/4-inch (2 mm ID) all-glass column packed with 3% OV-17 on Gas-Chrom Q (60-80 mesh). Other pertinent instrument conditions are given in Table 11. These conditions corresponded exactly to those used by the mass spectrometry laboratory and the sample preparation team, making it possible to compare relative retention times. Peaks exceeding the 1 ppb level in water ($\sim$10 ng/μl in extracts) were identified by peak integration values. Once these peaks were identified, quantitation was accomplished by converting the integration units to ng/μl and then calculating the concentration in the original water samples on the basis of the known extraction efficiencies in the sample preparation step.

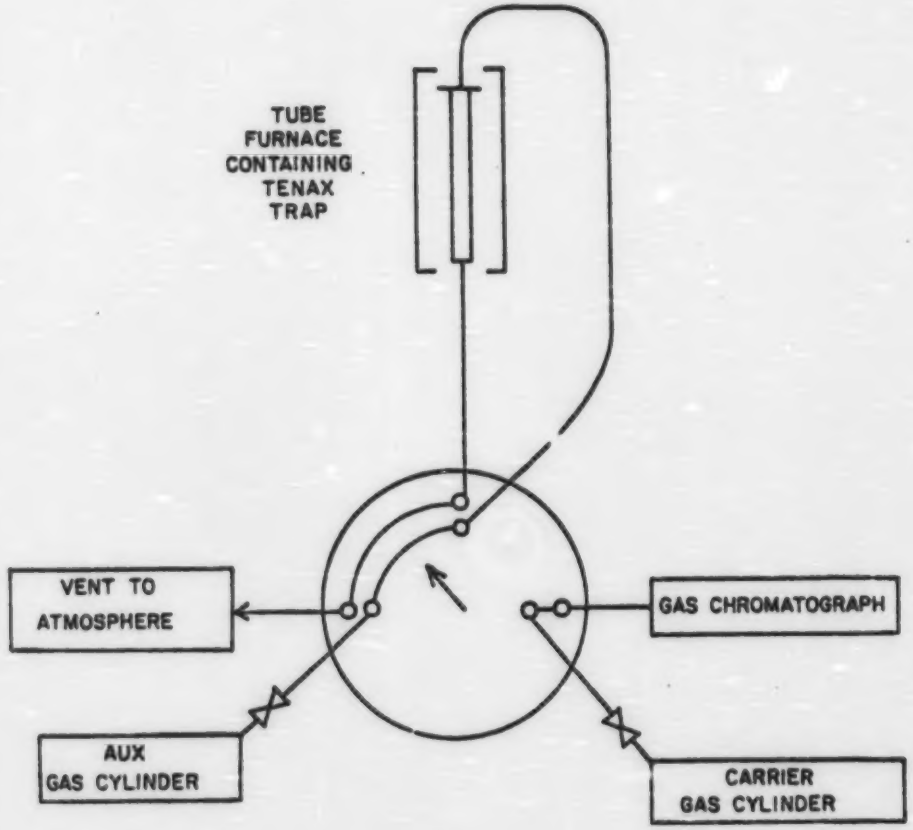


Figure 23. Schematic diagram of volatile organic elution system.

Table 11

Gas Chromatograph Column Conditions*

Initial temperature	35° C
Initial time	5.0 min.
Programming rate	10° C/min
Final temperature	300° C
Injector temperature	275° C
Detector temperature	350° C
Carrier gas flow	40 ml/min

*12 ft. x 1/4 in. (2 mm ID) all-glass column packed with 3% OV-17 on Gas-Chrom Q (60-80 mesh).

After two months, all quantitations were performed on a new Hewlett-Packard-Model 5711 gas chromatograph equipped with a Model 3380A reporting integrator. This instrument was used routinely to quantitate the balance of the samples collected. The procedure was modified slightly to make the best use of this new instrument and to shorten analysis times. The initial five-minute isothermal hold at 35° C was reduced to four minutes and the initial temperature was increased to 50° C. These changes reduced the tailing of the solvent peak and generally improved the characteristics of the total chromatogram. The temperature programming rate was decreased from 10° C/min to 8° C/min to improve resolution of peak clusters in the chromatograms. All other conditions remained unchanged.

Volatile samples were chromatographed on a 12-foot, all-glass column (2 mm ID) packed with 0.4% Carbowax 1500 on Carbopack C (Supelco, Inc., Bellefonte, Pa.). This column was determined to have resolution, capacity, and thermal stability (bleed) characteristics superior to the other column packings traditionally used for volatiles (e.g., Porapacks, Chromasorbs, etc.). For quantitation purposes, the Tenax trap was heated to 250° C and stripped for six minutes with a nitrogen carrier gas flow of 40 ml/min onto the Carbowax column held at 30° C (Figure 23). After purging, the trap was isolated from the column by changing the position of the valve. The column temperature was programmed to increase from 30° C to 200° C at 8° C/min and then held at 200° C for an additional 6 minutes. The injector and detector temperatures were maintained at 250° C.

Because of early problems encountered in the other laboratories with contamination from the gas valving system, the possibility of using a high-temperature valve when analyzing the stripped samples was investigated. Initially, the traps were heated to 250° C while the valve remained at 30 to 70° C. This temperature difference affected the purity of the stripping blanks and could have been a potential source of cross-contamination of volatiles from one run to the next. A new Valvco two-position, six-port valve which can be heated to 200° C was therefore substituted, making it possible to heat both the Tenax GC trap and the valve during analysis. The new valve had other advantages as well in that the carrier flow to the GC column was not interrupted and the column was never exposed to the atmosphere. Also, traps could be swept with carrier gas before connecting them to the GC column, again eliminating exposure of the column to the atmosphere. Finally, the valve material was stable at high temperatures, which helped to eliminate some of the peaks in the stripping blanks believed to originate in the Teflon gaskets of the original valves used.

The only difference between the procedures used by the quantitation and identification laboratories was in the method of heating the traps. In the quantitation laboratory, a combustion-tube furnace commercially available from A. H. Thomas was used rather than a hand-made tube heater. Evaluation of the tube furnace showed that it had several advantages: (1) the dimensions of the furnace accommodated the entire length of the trap in the heated zone; (2) the temperature of the furnace at a given potentiometer setting was highly reproducible; (3) the temperature variation along the length of the heated zone was negligible; (4) traps could be inserted and removed for cooling in seconds; and (5) the internal temperature of room-temperature traps inserted into the furnace rose to 250° C in two minutes or less.

Increasing the quantity of water sample stripped from 5 ml to 125 ml also simplified the analysis of the volatile samples by eliminating many of the significant contamination problems encountered in the early stages of this project. None of the fluorinated hydrocarbon species believed to have come

from the sampling valve were identified in any of the samples at the equivalent 1 ppb level or above after increasing the volume of sample stripped. The quality of the system blanks, which include bleed peaks from the Tenax GC trap matrix, was also improved. Figure 24 is a reproduction of a typical system blank. All of the peaks observed in the blank are well below the 1 ppb level. The first two peaks are methanol and ethanol. These substances are observed in every volatile sample by gas chromatography but are not seen in the GC/MS runs because they are vented out with the water. Peaks 3 through 5 are acetone, benzene, and toluene, respectively. Peak 6 is due to column bleed.

Quantitation of the volatile organics was accomplished by determining individual relative response factors for each of the commonly occurring volatile substances observed in the samples collected. The estimated concentrations of these compounds were corrected for these factors prior to the preparation of this report.

Selection of Internal Standards for the Acid- and Base-Extractable Fractions

To increase the accuracy of the quantitative data obtained on the acid- and base-extractable organics and to maintain consistent control of laboratory extraction procedures, internal standards were sought for both the acid and base extraction steps. The criteria used in selection were (1) gas chromatographic retention time, (2) purity, (3) mass spectral characteristics, (4) extraction efficiency at pH $\sim$12 or pH$\sim$2 with chloroform, (5) chemical and biological stability, and (6) occurrence in surface water samples.

Since it was known that hydrocarbon-type materials extract readily at basic pH, the cyclic hydrocarbon camphor was selected for the base extraction step. Likewise, fatty-acid-type compounds were known to be characteristic of the pH 2 extractables. Therefore, a branched-chain C_6 fatty acid (2-ethyl hexanoic acid) was selected for the acid internal standard. Both camphor and 2-ethyl hexanoic acid extraction efficiencies were determined on each group of samples processed. The average extraction efficiencies observed were 67% and 69%, respectively. These factors were used in correcting the quantitative data for the corresponding fractions. The 2-ethyl hexanoic acid served the added function of providing a check on the efficiency of the methylation step as well.

Figure 24. Gas-chromatographic trace of a representative system blank.

Since both camphor and napthalene, another compound considered as an internal standard, had previously been reported as constituents of certain surface water samples, an investigation was begun to find an alternative compound which would not be expected in nature and which would meet the criteria listed above. Several brominated compounds were evaluated:

Bromobenzene
Bromocyclohexane
Bromoheptane
Bromopentane
Bromononane
Bromodecane
Bromotetradecane
p-Bromo-Anisole
α-Bromo-Toluene
α-Bromo-*p*-Xylene

A number of the compounds were determined to be unsatisfactory based on the selection criteria above. The last three compounds in the list all had retention times in a good range, were of high purity, gave distinctive mass spectra, and had extraction efficiencies in a satisfactory range. When these compounds were tested for chemical stability in chloroform and surface water, however, the bromo compounds decomposed or reacted with compounds in the water. Other brominated compounds were considered, but none was found which met the criteria.

Investigation of Gas Chromatographic Methods for Monitoring Amines

Pure samples of six selected amines were obtained for analysis:

Aniline
Benzidine
β-Naphthylamine
o-Tolidine
o-Toluidine
Phenyl Hydrazine

The initial work was directed toward determining whether the extraction and separation techniques being used for this project would be able to detect these amines if they were present in any of the water samples.

A liter of ultrapure water was spiked with a pure amine compound at a level of 100 ppm, 1 ppm, or 50 ppb. Samples were prepared in triplicate. Once the amine was dissolved completely, the pH was adjusted to between 11

and 12. The sample was then extracted with a total of 200 ml of chloroform in three portions (100, 50, and 50 ml). The amount of the amine recovered in the chloroform was then determined either by direct weighing of the residue after removal of the solvent or by quantitation of the amine by gas chromatography. The extraction efficiencies determined are reported in Table 12.

Table 12
Extraction Efficiencies of Selected Amines

Amine	% Recovery*		
	100 ppm	1 ppm	50 ppb
Aniline	85.3	83.7	84.0
Benzidine	99.9	99.9	99.8
β-Naphthylamine	47.7	46.8	46.7
O-Tolidine	82.2	83.1	82.7
Phenyl Hydrazine	73.2	75.1	74.8
o-Toluidine	87.5	87.2	86.8

*Average of triplicate determinations.

Next, the relative retention times of these six amines were determined against the retention time of camphor using the gas chromatographic conditions routinely used for this project. Relative response factors for each amine (integrator counts/ng of amine divided by integrator counts/ng of camphor) were also determined using solutions of known concentration on the OV-17 column used for this project. The values are reported in Table 13.

Five other gas chromatographic column packings for the analysis of amines were evaluated using the six selected amines. Chromasorb 103, 4% Carbowax 20M + 0.8% KOH on Carbopack B, 4% Carbowax 20M + 1% Polypropyleneimine on Carbopack B, and 0.1% SP-1000 on Carbopack C columns were tested. In each case, the retention times of all of the amines being studied were too long or the compounds were not eluted at all. Relative retention times of the six amines selected for study were determined against the retention time of camphor using 10% Apiezon L/2% KOH on 80/100 mesh Chromasorb WAW. Relative response factors were also determined using solutions of known concentration. The results are presented in Table 14.

Table 13

Relative Retention Times and Relative Response Factors
For Selected Amines on 3% OV-17

Amine	Relative Retention Time[1]	Relative Response Factor[2]
Aniline	0.77	0.96
Benzidine	2.48	0.75
β-Naphthylamine	1.72	1.45
o-Tolidine	2.65	1.39
Phenyl Hydrazine	1.38	0.36
o-Toluidine	0.93	0.96

[1] Calculated relative to the retention time of camphor (10.84 min).
[2] Calculated relative to the response per nanogram of camphor (1650/ng).

Table 14

Relative Retention Times and Relative Response Factors
For Selected Amines on 10% Apiezon L/2% KOH

Amine	Relative Retention Time[1]	Relative Response Factor[2]
Aniline	0.746	0.695
Benzidine	2.425	0.693
β-Naphthylamine	1.638	0.655
o-Tolidine	3.180	0.715
o-Toluidine	0.919	0.761
Phenyl Hydrazine	1.500	0.014[3]

[1] Calculated relative to the retention time of camphor (14.19 min).

[2] Calculated relative to the response per nanogram of camphor (3409/ng).

[3] Coloration of sample and multiple peaks in chromatogram suggest some chemical and/or thermal degradation.

Both the OV-17 column and the Apiezon L/KOH column gave very satisfactory separation of the amines selected. The response per nanogram of material injected on column, however, was significantly higher using the deactivated Apiezon packing, indicating that some of the amine material was adsorbed to the OV-17 column packing. In survey studies such as the one just completed, a good approach may be to use the deactivated packings for quantitation and the OV-17 packing for mass spectrometry, since the bleed characteristics of the latter are more favorable than those of Apiezon L.

A major effort was directed toward evaluating the potential of a nitrogen-specific flame ionization detector (NFID) for amine analysis. A prototype conversion kit NFID detector was installed in the Hewlett-Packard 5710 gas chromatograph. The detector specifications state that a response discrimination factor of 5000 to 1 for nitrogen-containing vs. nonnitrogen-containing compounds can be achieved. This selectivity makes the NFID detector system ideal for screening water sample extracts (which may contain hundreds of organic compounds) for those that contain nitrogen. In practice, the NFID device was variable in response and had to be tuned and checked with standards frequently. When the device was operating properly, however, 0.1 ng of an amine (aniline) could be detected reproducibly at a relatively insensitive attenuation. New devices which are easier to maintain and which are more sensitive are available and should be evaluated.

Studies of the recovery of selected amines on ion exchange resins using purified XAD-4 and Biorex 70 resins were initiated. The selective recovery of amines on ion-exchange resins and subsequent elution showed some promise as a technique for the analysis of amines as an alternative to extraction. Limited access to liquid chromatographic facilities, however, prevented any detailed studies in this area.

SUMMARY OF THE ORGANIC COMPOUNDS FOUND

J. C. Means

A comprehensive listing of all of the organic compounds identified in the 204 samples collected and analyzed during the project is presented in Tables 15 through 17.

In the acid-extractable fraction (Table 15) 110 compounds were identified. These compounds generally fell into the classes of alcohols, fatty acid methyl esters, phthalate esters, polycyclic and polyunsaturated hydrocarbons, hydrocarbons, substituted phenolics, and halogenated hydrocarbons. The compounds appearing the most frequently in the acid extracts were: methyl palmitate (183), methyl stearate (165), diethyl hexyl phthalate (132), C_{15} terpineol (56), and methyl myristate (47). Of these compounds, only the phthalate ester is a synthetic organic compound. The others are believed to be products of the decay of natural materials. The majority of the compounds identified, however, were of synthetic origin and many have been identified as toxic or carcinogenic.

In the base extractable fraction (Table 16), 89 compounds were identified. These compounds fell into the general classes of: phthalate esters, hydrocarbons, halogenated hydrocarbons, and polycyclic and polyunsaturated hydrocarbons. The compounds appearing the most frequently in the base extracts were: diethyl hexyl phthalate (132), dibutyl phthalate (84), C_{15} terpineol (55) and C_{10} terpineol (36). Of these, the two phthalate esters are widely used synthetic organics while the terpineols are believed to be natural products. Many of the compounds identified in the base extracts were of synthetic origin and many of these have been identified as toxic.

Eighty-one purgeable organic compounds were identified in the 204 samples collected (Table 17). The majority of the compounds were halogenated hydrocarbons from C_1 to C_6. The compounds appearing the most frequently in the purgeable fraction were: chloroform (178), trichloroethylene (88), tetrachloroethylene (77), 1,2 dichloroethane (53), benzene (40), acetone (33), dichloromethane (32), toluene (31), and bromo-dichloromethane (24). It is significant that chloroform and many of the other chlorinated and brominated hydrocarbons appeared in almost every sample but at levels below 1 ppb. These compounds are now suspected carcinogens or are known to be toxic. Their widespread occurrence in surface waters emphasizes the need for further study of the origin and impact of these highly mobile substances in the environment.

Table 15

List of Acid-Extractable Compounds Found in 204 Water Samples and Their Frequency of Occurrence

Compound Name	Frequency
C_6 Alcohol	1
C_7 Alcohol	2
C_8 Alcohol	3
C_9 Alcohol	5
C_{10} Alcohol	6
C_{11} Alcohol	7
C_{12} Alcohol	7
C_{13} Alcohol	8
C_{14} Alcohol	9
C_{15} Alcohol	9
C_{16} Alcohol	9
C_{17} Alcohol	9
C_{18} Alcohol	9
C_{19} Alcohol	6
C_{20} Alcohol	7
C_{21} Alcohol	6
C_{22} Alcohol	6
C_{23} Alcohol	4
C_{24} Alcohol	3
C_{25} Alcohol	1
C_{26} Alcohol	1
Alkyl Benzene	3
($C_{18}H_{12}$) Benzoanthrene	1
Butylbenzyl Phthalate	3
Butyl Phthalyl Butyl Glycolate	23
Caffeine	1
$C_xH_yCl_z$, $x \geq 4$, $z \geq 5$ Isomers	12
C_8H_{16} Isomer	1
$C_{10}H_{10}$ Isomer	1
$C_{15}H_{24}$	1

Table 15, cont.

Compound Name	Frequency
$C_{16}H_{10}$ Isomer	1
$C_{16}H_{10}$ (Pyrene)	3
$C_{21}H_{32}O_2$ Methyl Pimarate Isomer	8
Dibutyl Phthalate	15
Dichlorinated Hydrocarbon C - 5	2
Dichlorobutane	11
Dichloroheptane	1
Diethyl Hexyl Phthalate	132
Diisobutyl Phthalate	2
Dioctyl Adipate	6
Dioctyl Phthalate	1
Diphenyl Dulfone	1
Fatty Acid Methyl Ester C $\geq$ 10	1
Fatty Acid Methyl Ester C $\geq$ 12	7
Fatty Acid Methyl Ester C $\geq$ 13	1
Fatty Acid Methyl Ester C = 14	3
Fatty Acid Methyl Ester C $\geq$ 14	15
Fatty Acid Methyl Ester C $\geq$ 15	7
Fatty Acid Methyl Ester C $\geq$ 16	11
Fatty Acid Methyl Ester C $\geq$ 17	2
Fatty Acid Methyl Ester C $\geq$ 18	5
Fatty Acid Methyl Ester C $\geq$ 19	2
Fatty Acid Methyl Ester C $\geq$ 20	14
Fatty Acid Methyl Ester C $\geq$ 21	1
Fatty Acid Methyl Ester C $\geq$ 22	18
Fatty Acid Methyl Ester C $\geq$ 23	1
Fatty Acid Methyl Ester C $\geq$ 24	11
Fatty Acid Methyl Ester C $\geq$ 26	3
Hexachlorobenzene	2
Hexachlorobutadiene	2
Hexachlorobutene	2
Hexachloroethane	1
Hexachloro-hexafluoropentane	1

Table 15, cont.

Compound Name	Frequency
Hydrocarbon C $\geq$ 8	3
Hydrocarbon C $\geq$ 10	4
Hydrocarbon $\geq$ 12	3
Hydrocarbon C $\geq$ 14	4
C_{15} Hydrocarbon	2
Hydrocarbon C $\geq$ 16	7
C_{16} Hydrocarbon	2
C_{17} Hydrocarbon	2
Hydrocarbon C $\geq$ 18	11
Hydrocarbon C $\geq$ 20	7
Hydrocarbon C $\geq$ 22	10
Hydrocarbon C $\geq$ 24	4
Hydrocarbon C $\geq$ 26	5
Hydrocarbon C $\geq$ 28	4
Hydrocarbon C $\geq$ 30	5
Methoxy Carbonyl Benzophenone	1
Methyl Arachidate	2
Methyl-2(4-chlorophenoxy) Butanoate	13
Methyl Dehydroabietate	11
Methyl Dichlorophenoxy Acetate	4
Methyl Dichlorophenyl Ether	1
Methyl-2, 2-Dichloro-3-Methyl Butanoate	1
Methyl Laurate	7
Methyl Myristate	47
Methyl Naphthoate	1
Methyl Palmitate	183
Methyl Pentachlorophenyl Ether	12
Methyl Pentachlorophenoxy Ether	2
Methyl Stearate	165
Methyl Tetrachlorophenyl Ether	1
2-Methyl Thiobenzothiazole	1
Methyl-Trichlorophenoxy Acetate	1
Methyl Trichlorophenyl Ether	5
Pentachloroanisole	10

Table 15, cont.

Compound Name	Frequency
Pentachlorobutadiene	2
Pentachlorobutene	3
Pentachloroethane	3
Tetrachlorobutadienne	3
C_{15} Terpene	37
C_{10} Terpineol	27
C_{15} Terpineol	56
Tetrachloroanisole	4
Trichloroanisole	3
Trichloroheptane	1
Trichlorohexane	3
Trichloropentane	4
Unidentified Phthalate	2

Table 16

List of Base-Extractable Compounds Found in 204 Water Samples and Their Frequency of Occurrence

Compound Name	Frequency
Alkyl Acid Ester ($R + R^1 \geq 8$)	3
Alkyl Phenyl Ether	1
Anthracene	1
Atrazine	5
Benzothiazole	2
Biphenyl	1
Bromopropyl Benzene	1
Butylbenzyl Phthalate	2
Butyl Phthalyl Butyl Glycolate	17
Caffeine	9
C_{10} Camphenol	2
$C_xH_yCl_z$, $x \geq 4$, $z \geq 5$ (series of isomers)	5
$C_5H_{10}Cl_2$	1
C_8H_{16} Isomer	1
$C_{16}H_{10}$ (Pyrene)	7
$C_{18}H_{12}$	3
$C_{22}H_{14}$	1
Chloro-Nitrobenzene	3
Chloroprene Dimer	1
Chloroprene	1
Dibromo-chloroethane	1
Dibromoethane	1
Dibutyl Nonanedioate	1
Dibutyl Phthalate	84
Dichlorobenzene	9
Dichlorobutane	19
Dicyclohexyl Phthalate	1
Diethoxyethane	4
N,N-Diethylaniline	1

Table 16, cont.

Compound Name	Frequency
Diethyl Hexyl Phthalate	132
Diethyl Phthalate	6
Diisobutyl Nonanedioate	1
Diisobutyl Phthalate	5
Dimethyl Biphenyl	1
Dimethyl Naphthalene	2
Dimethyl Styrene	1
Dinitrotoluene	2
Dioctyl Adipate	2
Diphenyl Benzene	1
Diphenyl Ethane	1
Diterpene $C_{10}H_{16}$	4
Hexachlorobenzene	1
Hexachlorobutadiene	2
Hexachlorobutene	2
Hexachloroethane	2
Hydrocarbon $C \geq 8$	1
Hydrocarbon $C \geq 10$	1
Hydrocarbon $C \geq 12$	5
Hydrocarbon $C \geq 14$	10
C_{15} Hydrocarbon	1
C_{16} Hydrocarbon	2
Hydrocarbon $C \geq 16$	16
C_{18} Hydrocarbon	3
Hydrocarbon $C \geq 18$	8
Hydrocarbon $C \geq 20$	16
Hydrocarbon $C \geq 22$	13
Hydrocarbon $C \geq 24$	11
Hydrocarbon $C \geq 26$	7
Hydrocarbon $C \geq 28$	7
Hydrocarbon $C \geq 29$	1
Hydrocarbon $C \geq 30$	7
Hydrocarbon $C \geq 31$	1

Table 16, cont.

Compound Name	Frequency
Hydrocarbon $C \geq 32$	1
Hydrocarbon $C \geq 33$	1
Hydrocarbon $C \geq 34$	1
Hydrocarbon $C \geq 35$	1
Hydroxy-borneol	1
Indole	1
Methyl Acenaphthene	1
Methyl Naphthalene	2
2-Methyl Thiobenzothiazole	1
Nitrotoluene	3
Pentachlorethane	2
Pentachlorobutadiene	3
Pentachlorobutene	2
Phenanthrene	1
Terpene C_{15}	1
Terpineol C_{10}	36
Terpineol C_{15}	55
Tetrachlorobutadiene	3
Tetrachloroethane	2
Tetrachloroethylene	4
Trichloroethylene	1
Tritepene $C_{15}H_{24}$	3
Unidentified Phthalate	6
Xylene	1

Table 17
List of Volatile Compounds Found in 204 Water Samples and Their Frequency of Occurrence

Compound Name	Frequency
Acetone	33
Acetophenone	6
Benzaldehyde	1
Benzene	40
Bromobenzene	9
1-Bromo-1-Chloroethane	2
1-Bromo-2-Chloroethane	1
1-Bromo-2-Chloropropane	1
Bromo-Dichloroethane	2
Bromo-dichloromethane	24
Bromo-Trichloropropane	1
Butadiene	1
Butanal	1
Butane	3
Butene	5
C_5H_8O or $C_6H_{12}O$	11
$C_5H_{10}O$ or $C_6H_{12}O$	2
C_8H_{17}	1
Carbon Tetrachloride	6
Chlorobenzene	11
1-Chloro-2-Bromoethane	1
1-Chloro-2-Bromopropane	1
Chloroform	178
Chloroprene	1
Cyclohexane	13
Cyclopentane	1
Dibromo-Chloromethane	10
Dibromoethane	2
Dichlorobenzene	23

Table 17, cont.

Compound Name	Frequency
1,2-Dichloroethane	53
Dichloroethylene	19
Dichloro-Iodomethane	1
Dichloromethane	32
1,2-Dichloropropane	8
Diethyl Ether	9
Diisopropyl Ether	2
Dimethoxymethane	10
Dimethyl Sulfide	1
Dimethyl Disulfide	5
Dimethylformamide	1
Dioxane	4
Dioxolane	1
Ethanethiol	1
Ethyl Acetate	1
Ethylbenzene	5
Ethyl Methyl Dioxolane	5
Fluoro-dichloro-bromomethane	1
Freon	1
Furfural	1
Heptene	1
Hexane	14
Hexanol	1
Hexene Isomers	5
Methacrylonitrile	1
Methyl-t-Butyl Ketone	1
Methyl Ethyl Ketone	1
Methyl-isobutyl Ketone	2
Methyl Methacrylate	1
2-Methyl Propanal	1
Methylal	1
4 Methyl-2-Ethyl-1,3-Dioxolane	2
Methyl-tetrahydrofyran	2
Neopentane	1

Table 17, cont.

Compound Name	Frequency
Nonene	1
Pentane	18
Pentene Isomer	4
C_{10} Terpene	2
1,1,2,2-Tetrachloroethane	12
Tetrachloroethylene	77
Tetrahydrofuran	29
Tetrahydropyran	4
Toluene	31
Tribromomethane	5
Trichlorobutane	1
Trichloroethane	11
1,1,1-Trichloroethane	18
Trichloroethylene	88
Trichloropropane	6
Trichloro-fluoromethane	11
Trichloro-trifluoroethane	8

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